...NOE LIBRARY

Volume 40 August, 1935 Number 2

SOIL SCIENCE

Editor-in-Chief
JACOB G. LIPMAN

Associate Editor
HERMINIE BROEDEL KITCHEN

Contents

The Clay Content of the Soil as Related to Climatic Factors, Particularly Temperature. HANS JENNY 111

Sorption of Phosphates by Non-Calcareous Hawaiian Soils. L. E. DAVIS .. 129

A New Method of Estimating Exchangeable Bases in Soils. AMAR NATH PURI 159

A Comparison Between the Suction Method and the Centrifuge Method for Determining the Moisture Equivalent of Soils. GEORGE JOHN BOUYOUCOS 165

A Machine for the Subsurface Treatment of Soils with Chloropicrin and with Carbon Bisulfide for Nematode Control under Field Conditions. J. R. NELLER and R. V. ALLISON 173

A Comparative Study of the Bacterial Flora of Windblown Soil: VI. Death Valley, California, with Summary of Six Soil Studies. LAETITIA M. SNOW 181

Published Monthly by THE WILLIAMS & WILKINS COMPANY
MT. ROYAL AND GUILFORD AVENUES, BALTIMORE, MARYLAND, U. S. A.

Made in United States of America

SOIL SCIENCE

FOUNDED BY
RUTGERS COLLEGE
NEW BRUNSWICK, N. J.

ADVISORY STAFF

A. W. Blair, J. S. Joffe, L. L. Lee, H. C. McLean, G. T. Nightingale, A. L. Prince, J. W. Shive, H. B. Sprague, R. L. Starkey, and S. A. Waksman, New Jersey Agricultural Experiment Station, New Brunswick, N. J.

CONSULTING EDITORS

F. J. ALWAY
University of Minnesota, St. Paul, Minn.

K. ASO
Imperial University, Tokyo, Japan

C. BARTHEL
Lantbrukshögskolan, Uppsala, Sweden

RICHARD BRADFIELD
College of Agriculture, Ohio State University, Columbus, Ohio

P. E. BROWN
Iowa State College of Agriculture, Ames, Iowa

B. C. BURT
Imperial Council of Agricultural Research, New Delhi, India

H. J. CONN
New York State Experiment Station, Geneva, N. Y.

ALBERT DEMOLON
Ministry of Agriculture, Paris, France

E. B. FRED
University of Wisconsin, Madison, Wis.

V. V. GEMMERLING
Agronomitsheskii Institute, Moskovskii Universitat, Moscow, U. S. S. R.

J E. GREAVES
Utah Agricultural College, Logan, Utah

ACH. GREGOIRE
Agricultural Experiment Station, Gembloux, Belgium

B. L. HARTWELL
143 Armington St., Edgewood, R. I.

D. J. HISSINK
Soil Science Institute, Groningen, Holland

O. LEMMERMANN
Institut für Agrikulturchemie u. Bakteriologie der Landwirtschaftlichen Hochschule, Berlin-Dahlem, Germany

C. B. LIPMAN
University of California, Berkeley, Calif.

BURTON E. LIVINGSTON
Johns Hopkins University, Baltimore, Md.

HENRIK LUNDEGÅRDH
Centralanstalten för jordbruksförsök Stockholm, Sweden

T. L. LYON
Cornell University, Ithaca, N. Y.

M. M. MCCOOL
Boyce-Thompson Institute, Yonkers, N. Y.

W. H. MACINTIRE
University of Tennessee, Knoxville, Tenn.

S. MATTSON
Lantbrukshögskolan, Uppsala, Sweden

E. A. MITSCHERLICH
University of Königsberg, Prussia

C. A. MOOERS
University of Tennessee, Knoxville, Tenn.

D. N. PRIANISHNIKOV
Timiryazev Academy, Moscow, U. S. S. R.

THEO. REMY
Institut für Boden- und Pflanzenbaulehre, Bonn a. Rh., Prussia

G. ROSSI
Royal Agricultural High School in Portici, Naples, Italy

E. J. RUSSELL
Rothamsted Experimental Station, Harpenden, England

O. SCHREINER
U. S. Department of Agriculture, Washington, D. C

ALEXIUS A. J. DE'SIGMOND
Royal Hungarian Joseph University of Technical Sciences, Budapest, Hungary

J. STOKLASA
Technical High School, Prague, Czechoslovakia

CHAS. E. THORNE
Ohio Experiment Station, Wooster, Ohio

N. M. TULAIKOV
Agricultural Experiment Station, Saratov, U. S. S. R.

G. WIEGNER
Landwirtschaftliche Hochschule, Zürich, Switzerland

S. WINOGRADSKY
Pasteur Institute, Paris, France

Entered as second-class matter, May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879.

Copyright, 1935, The Williams & Wilkins Company

THE CLAY CONTENT OF THE SOIL AS RELATED TO CLIMATIC FACTORS, PARTICULARLY TEMPERATURE

HANS JENNY

University of Missouri[1]

Received for publication July 23, 1934

The study of soil formation on the basis of the functional concept aims to establish numerical relations (laws) between soil properties and soil forming factors with the aid of the equation

$$\text{soil} = f\,(m, T, v, p, r, t, \ldots) \qquad (A)$$

which means that a soil depends on moisture (m), temperature (T), vegetation (v), parent material (p), topography (r), time (t), etc.

In the present paper an attempt is made to correlate the average clay content of soils with climatic factors, particularly temperature. In other words the purpose of this study is to ascertain the nature of the function f in the equation

$$\text{clay} = f\,(\text{temperature})_{m, v, p, r, t, \ldots} \qquad (B)$$

where the subscripts indicate that all the major soil forming factors are to be kept constant.

SELECTION OF REGION

On the basis of equation (B), which requires constant soil forming factors, the selection of the area to be investigated should be guided by the following principles:

Keep parent material constant, e.g., restrict the study to igneous rocks, or loess, or limestone, etc.

Select soils of similar age but preferably not too young.

Select soils which have developed under comparable climatic moisture conditions (for instance, similar precipitation-evaporation ratios).

Control secondary soil forming factors such as vegetation and topography.

Vary temperature as much as possible.

No large district will be found that strictly meets the aforementioned requirements, but fortunately satisfactory approximations exist. In the eastern, humid part of the United States, an extensive region of igneous and

[1] Missouri Agricultural Experiment Station, Journal Series No. 386.

The author is indebted to Professor C. F. Shaw of the University of California for valuable suggestions and criticisms.

metamorphic rocks reaches from Maine to Alabama and comprises a temperature interval of over 12°C. annual temperature. For the last 30 years the area has been studied intensively by the Bureau of Chemistry and Soils, and numerous soils reports, maps, and mechanical analyses of soils have been published (2). These were taken as the basis for the present study. The counties chosen for the investigation of the clay-temperature relationships are shown in figure 1.

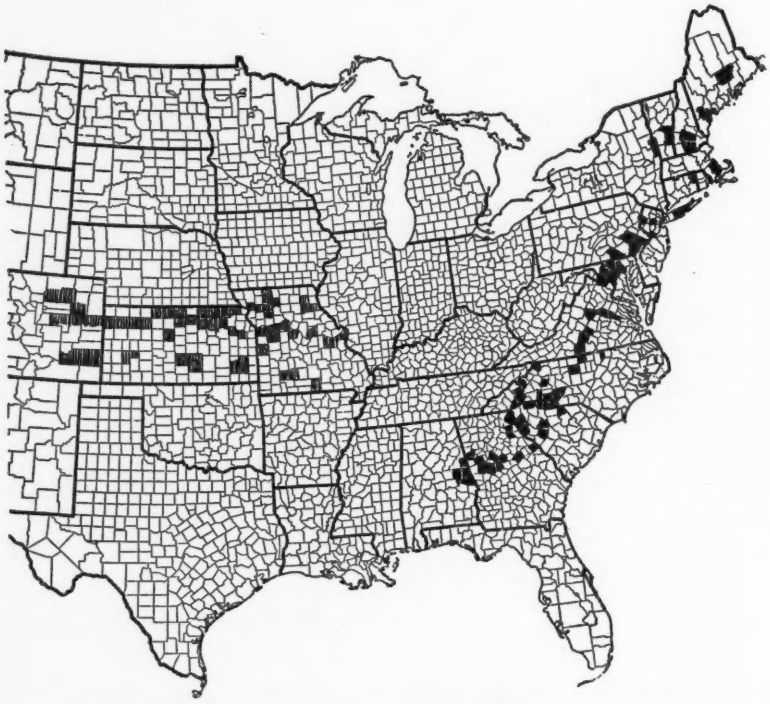


FIG. 1. MAP SHOWING THE LOCATION OF THE COUNTIES OR AREAS INVESTIGATED

Black areas refer to the clay-temperature study, shaded areas to the clay-rainfall series (5)

DESCRIPTION OF METHOD EMPLOYED

At least a thousand mechanical analyses of soils from the district chosen are to be found in the literature, but of these only 151 could be used in accordance with the requirements outlined. The analysis of the data was based upon the following considerations:

In order to avoid soils of mere local occurrence, only those types were included which cover more than 10 per cent of a county area. An exception was made in the case of basic rocks and gneisses in order to obtain enough figures to permit statistical treatment.

Only well-drained upland soils, originally timbered, were assembled.

The crystalline rocks were separated into the following groups: (a) granites, (b) gneisses, (c) schists, (d) basic rocks (gabbro, diorite). In a number of cases the exact nature of these groups could not be ascertained because the soil reports characterize the parent material only as "mixtures of granites and gneisses" or "mixtures of gneisses and schists," etc. Hence, the following additional groups were included: (e) granites and gneisses, (f) gneisses and

TABLE 1

Data for the parent material group (a) "granites"

Numbers 1–3 glacial soils; climatic data represent annual values

NUMBER	STATE	COUNTY OR AREA	TEMPERATURE	RAINFALL	N.S.Q.	SOIL TYPE	CLAY CONTENT
			°C.	*inches*			*per cent*
1	New Hampshire	Nashua	7.3	38.8	600	Gloucester stony loam	6.8
2	New Hampshire	Nashua	7.3	38.8	600	Gloucester stony sandy loam	16.8
3	Maine	Cumberland	7.9	42.2	520	Gloucester sandy loam	8.1
4	North Carolina	Mt. Mitchell	12.0	52.5	400	Porters sand	14.5
5	Virginia	Albemarle	12.7	36.9	500	Porters sand	13.5
6	Virginia	Albemarle	12.7	36.9	500	Cecil sandy loam	34.4
7	North Carolina	Henderson	12.9	62.2	400	Porters sandy loam	28.6
8	North Carolina	Henderson	12.9	62.2	400	Porters sand	10.9
9	North Carolina	Caswell	14.3	46.0	400	Durham coarse sandy loam	31.0
10	North Carolina	Cleveland	15.3	53.1	400	Cecil sandy clay loam	48.1
11	South Carolina	Oconee	15.6	53.6	380	Cecil fine sandy loam	25.0
12	South Carolina	Oconee	15.6	53.6	380	Porters fine sandy loam	18.6
13	South Carolina	Cherokee	15.7	48.6	350	Cecil sandy loam	41.4
14	South Carolina	Cherokee	15.7	48.6	350	Cecil sand	24.0
15	South Carolina	Abbeville	16.3	47.6	300	Cecil sandy loam	33.1
16	South Carolina	Lancaster	16.5	44.1	350	Cecil gravelly loam	24.6
17	South Carolina	York	16.8	49.8	300	Cecil fine sandy loam	40.2
18	South Carolina	York	16.8	49.8	300	Cecil sand	39.7
19	Alabama	Chambers	17.2	50.9	300	Cecil clay loam	31.7

schists, (g) granites, gneisses, and schists. To economize in space, individual data are presented only for the groups (a), (b), (d), and (g). (*See* tables 1–4.)

The "per cent clay" figures refer to the average clay content of a soil profile from the surface to a depth of 36–40 inches (92–102 cm.), calculated as previously (5) by the formula

$$\text{Per cent clay} = \frac{S_1 + 3S_2}{4} \qquad (C)$$

where S_1 represents the clay content of the surface soil and S_2 that of the subsoil.

The term "clay" includes all particles having a diameter smaller than 5μ

TABLE 2

Data for the parent material group (b) "gneisses"

Climatic data represent annual values

NUMBER	STATE	COUNTY OR AREA	TEMPERATURE	RAINFALL	N.S.Q.	SOIL TYPE	CLAY CONTENT
			°C.	*inches*			*per cent*
1	Pennsylvania	Berks	10.7	44.5	340	Chester loam	27.1
2	Pennsylvania	Chester	10.8	49.3	400	Chester loam	22.3
3	Pennsylvania	Chester	10.8	49.3	400	Brandywine loam	18.8
4	North Carolina	Transylvania	12.8	63.7	400	Porters sandy loam	22.7
5	Virginia	Campbell	13.8	41.8	320	Iredell	23.6
6	Virginia	Pittsylvania	14.9	42.1	350	Durham fine sandy loam	18.9
7	South Carolina	Oconee	15.6	53.6	380	Cecil clay	32.8
8	South Carolina	Oconee	15.6	53.6	380	Porters clay	38.8
9	Georgia	Coweta	16.7	50.9	320	Cecil sandy loam	33.1
10	Georgia	Oconee	16.7	48.1	320	Cecil sandy clay loam	36.3
11	South Carolina	Saluda	17.4	47.6	300	Cecil clay	42.5
12	Georgia	Franklin	19.8	50.2	320	Cecil clay	45.5
13	Georgia	Franklin	19.8	50.2	320	Cecil sandy loam	29.1

TABLE 3

Data for the parent material group (d) "basic rocks"

Climatic data represent annual values

NUMBER	STATE	COUNTY OR AREA	TEMPERATURE	RAINFALL	N.S.Q.	SOIL TYPE	CLAY CONTENT
			°C.	*inches*			*per cent*
1	New Jersey	Bernardsville	10.0	48.4	400	Montalto silt loam	14.4
2	New Jersey	Belvidere	10.8	47.9	400	Montalto silt loam	13.9
3	New Jersey	Trenton	12.0	48.8	437	Cecil loam	22.3
4	Maryland	Montgomery	12.1	38.4	350	Conowingo silt loam	19.5
5	Virginia	Leesburg	12.2	40.3	450	Iredell clay loam	37.6
6	Maryland	Howard	12.8	42.7	316	Montalto clay loam	29.7
7	Maryland	Howard	12.8	42.7	316	Mecklenburg loam	18.7
8	Maryland	Baltimore	13.0	42.7	316	Mecklenburg loam	17.2
9	Maryland	Baltimore	13.0	42.7	316	Iredell silt loam	19.3
10	Maryland	Baltimore	13.0	42.7	316	Conowingo silt loam	17.7
11	North Carolina	Caswell	14.3	46.0	400	Iredell sandy loam	45.3
12	North Carolina	Cabarrus	15.1	46.9	300	Iredell fine sandy loam	41.6
13	North Carolina	Cabarrus	15.1	46.9	300	Mecklenburg clay loam	45.0
14	North Carolina	Cabarrus	15.1	46.9	300	Mecklenburg sandy loam	35.8
15	North Carolina	Mecklenburg	15.6	46.9	300	Iredell fine sandy loam	32.9
16	North Carolina	Mecklenburg	15.6	46.9	300	Mecklenburg clay loam	41.9
17	North Carolina	Mecklenburg	15.6	46.9	300	Mecklenburg loam	42.7
18	North Carolina	Gaston	15.7	46.9	300	Iredell clay loam	32.6
19	South Carolina	Abbeville	16.3	47.6	300	Iredell clay loam	41.5
20	South Carolina	York	16.8	49.8	300	Iredell clay loam	39.7
21	Georgia	Meriwether	16.8	48.9	300	Davidson clay	51.1

(dispersion with ammonia). Compared with modern technique of mechanical soil analyses the values are consistently somewhat low, but are comparable

TABLE 4

Data for the parent material group (g) *"granites, gneisses, and schists"*

Numbers 1–7 are glacial soils; climatic data represent annual values

NUMBER	STATE	COUNTY OR AREA	TEMPERATURE	RAINFALL	N.S.Q.	SOIL TYPE	CLAY CONTENT
			°C.	*inches*			*per cent*
1	Maine	Orono	6.3	42.3	520	Bangor loam	16.0
2	New Hampshire	Nashua	7.3	38.8	600	Gloucester stony loam	6.8
3	New Hampshire	Nashua	7.3	38.8	600	Gloucester stony sandy loam	16.8
4	New Hampshire	Merrimack	7.3	38.8	600	Gloucester stony loam	12.9
5	New Hampshire	Merrimack	7.3	38.8	600	Gloucester stony sandy loam	5.9
6	Connecticut	Windham	8.3	43.9	450	Gloucester stony fine sandy loam	5.5
7	Connecticut	Windham	8.3	43.9	450	Gloucester fine sandy loam	6.2
8	North Carolina	Ashe	8.9	60.2	400	Ashe loam	15.1
9	North Carolina	Ashe	8.9	60.2	400	Porters clay loam	23.9
10	Pennsylvania	Montgomery	11.8	44.9	400	Chester loam	25.3
11	North Carolina	Mt. Mitchell	12.0	52.5	400	Porters clay	30.3
12	North Carolina	Mt. Mitchell	12.0	52.5	400	Porters black loam	22.5
13	North Carolina	Mt. Mitchell	12.0	52.5	400	Porters sandy loam	21.2
14	North Carolina	Henderson	12.9	62.2	400	Porters loam	28.9
15	North Carolina	Caswell	14.3	46.0	400	Cecil sandy loam	34.5
16	North Carolina	Hickory	14.6	49.5	400	Cecil sandy loam	31.3
17	North Carolina	Hickory	14.6	49.5	400	Cecil clay	35.7
18	North Carolina	Hickory	14.6	49.5	400	Porters sandy loam	34.5
19	North Carolina	Mecklenburg	15.6	46.9	300	Cecil clay loam	36.4
20	North Carolina	Mecklenburg	15.6	46.9	300	Cecil sandy loam	34.8
21	North Carolina	Mecklenburg	15.6	46.9	300	Cecil clay	57.5
22	North Carolina	Mecklenburg	15.6	46.9	300	Cecil fine sandy loam	41.5
23	South Carolina	Oconee	15.6	56.7	380	Porters loam	28.9
24	North Carolina	Gaston	15.7	46.9	300	Cecil sandy loam	30.9
25	North Carolina	Gaston	15.7	46.9	300	Cecil coarse sandy loam	43.5
26	South Carolina	Campobello	15.8	44.0	300	Cecil clay	50.0
27	South Carolina	Abbeville	16.3	47.6	300	Cecil clay	40.0
28	South Carolina	York	16.8	50.0	300	Cecil clay	52.5
29	Georgia	Spalding	16.9	44.1	320	Cecil clay	53.3
30	Georgia	Pike	17.2	51.0	300	Cecil sandy loam	37.2
31	Alabama	Lee	18.4	51.0	300	Cecil sandy loam	31.0

among themselves. The fact that the samples were collected and analyzed over a period of 30 years tends to eliminate accumulation of systematic errors.

All data reported in tables 1–4 refer to but single profiles except in a few cases which are averages of two or three samples.

AVERAGE SOIL CLAY LEVELS IN NORTHEASTERN AND SOUTHEASTERN UNITED STATES

The average clay contents of the soils of the northern (latitude 35–45°N) and southern parts (latitude 30–35°N) of the region investigated differ remarkably, as shown in table 5. The northern clay level contains 16.3 per cent clay, the southern has a value of 38.0 per cent, a difference amounting to 21.7 per cent ± 1.77, which is statistically highly significant. Generally speaking, *the southern soils contain about 2.33 times more clay than the northern ones.*

TABLE 5

Clay levels of northern and southern latitudes

Depth 0–3 feet

LATITUDE	TEMPERATURE RANGE	GEOGRAPHIC REGION (STATES)	NUMBER OF PROFILES	AVERAGE CLAY CONTENT
	°C.			*per cent*
35°–45°	6–12	New England States, New York, Pennsylvania, New Jersey, Maryland, North Carolina. (Glaciated and unglaciated region)	39	16.3 ±1.18*
30°–35°	16–19	South Carolina, Georgia, Alabama	33	38.0 ±1.30

* Mean error.

THE CAUSES OF THE DIFFERENT CLAY LEVELS IN NORTHERN AND SOUTHERN LATITUDES

In table 5 are given the annual temperatures which correspond to the latitudes cited. It is evident that a decided parallelism between temperature intervals and clay levels exists. In spite of such a correlation it is not permissible to conclude that temperature is solely responsible for the observed differences in the clay content of the soils. A number of soil forming factors have not been rigidly controlled, and a glance at the tables 1–4 indicates that such variables as age (glaciation influence) type of igneous rocks, erosion, and fluctuating moisture need careful consideration before the rôle of temperature can be evaluated in a quantitative manner.

The factor age (influence of glaciation)

Throughout the Pleistocene the greater part of the Piedmont Plateau has been free from glaciation. The New England States were covered by the last ice sheet, but since the retreat of the ice masses soil formation could have been proceeding for at least ten to twenty thousand years. Indeed, in certain localities mature profiles have been developed (podzols). Furthermore, it is very

likely that the mechanical grinding of the moving glaciers has augmented the clay content of these "glaciated soils," which are derived from ground moraines made up of igneous rock debris. On the other hand, one might contend that glaciation has retarded clay formation and that the low clay levels of northern latitudes are due to the youthfulness of the soils rather than to environmental conditions. From the viewpoint of temperature inquiry it appears desirable to treat the soils of glaciated districts separately in order to avoid uncertainty in the interpretation of the data.

Table 6 shows the clay levels of the unglaciated area only. The differences in the clay contents of the soils for the selected intervals still persist. The northern Piedmont Region differs from the southern by 12.4 ±1.80 per cent, a value which again is statistically very significant.

Types of igneous and metamorphic rocks and their effect on clay formation

All soils which are assembled in tables 5 and 6 have been derived from igneous and metamorphic rocks. It is commonly believed that basic rocks

TABLE 6

Clay levels for various latitudes and temperature intervals

Glaciated areas excluded

LATITUDE	TEMPERATURE RANGE	GEOGRAPHIC REGION (STATES)	NUMBER OF PROFILES	AVERAGE CLAY CONTENT
	°C.			*per cent*
35–41°	10–13	Pennsylvania, New Jersey, Maryland, Virginia, North Carolina	38	25.6 ±1.24*
30–35°	16–19	South Carolina, Georgia, Alabama	33	38.0 ±1.30

* Mean error.

tend to weather faster than gneisses, and if the former are particularly abundant in the South, one would expect a relation exactly like that presented in tables 5 and 6. It becomes necessary to determine the clay levels for each of the separate groups of crystalline rocks, if possible by a series of continuous functions. Such correlations can indeed be observed as indicated by figures 2 and 3, which illustrate the relation between the clay content of the groups (d) and (g) and the latitude, the latter expressed on a temperature scale. The curves, fitted according to the method of least squares, follow the straight line equation:

$$\text{per cent clay} = a_1 T + b_1 \qquad (D)$$

where T represents the average annual temperature in centigrade and a_1, b_1 are constants.

. Similar relationships hold for the other groups of parent materials as seen from data in table 7, which contains the values of the constants of equation (D) and also the corresponding correlation coefficients. The latter—giving

due consideration to degrees of freedom—are very significant and prove definitely *that the clay content of soils derived from uniform parent materials increases in a regular manner from north to south.*

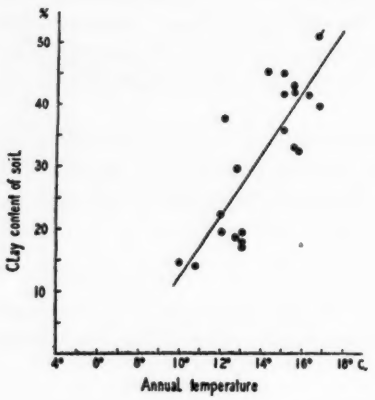


FIG. 2

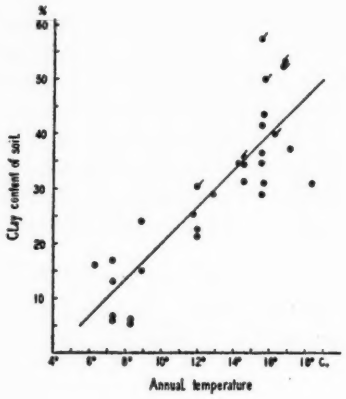


FIG. 3

FIG. 2. GENERAL NORTH-SOUTH CORRELATION BETWEEN CLAY CONTENT OF SOIL AND LATITUDE (ANNUAL TEMPERATURE)

Data refer to parent material group (d) or "basic rocks"

FIG. 3. GENERAL NORTH-SOUTH CORRELATION BETWEEN CLAY CONTENT OF SOIL AND LATITUDE (ANNUAL TEMPERATURE)

Data refer to parent material group (g) "granites, gneisses, and schists." Semi-black dots indicate soils derived from moraines.

TABLE 7

General north-south correlations

Data showing the type of parent material, correlation coefficients, and the values of the constants of equation (*D*).

NUMBER	PARENT MATERIAL	NUMBER OF PROFILES	a_1	b_1	CORRELATION COEFFICIENT r
a	Granites	19	2.64	−10.4	+0.700
b	Gneisses	13	2.02	−0.2	+0.717
c	Schists	22	2.66	−5.3	+0.756
d	Basic rocks	21	4.94	−37.5	+0.814
e	Granites and gneisses	27	3.58	−24.8	+0.707
f	Gneisses and schists	18	2.15	+2.6	+0.490
g	Granites, gneisses, and schists	31	3.33	−13.4	+0.856

The rôle of erosion

On account of specific cropping customs the problem of erosion assumes great magnitudes in the southern part of the region studied. The original soils were Cecil sand and Cecil sandy loam, the porous surface horizons resting

on subsoils of heavy clay. As a result of sheet erosion, much of the original surface soil or A horizon has been stripped away thus giving rise to large areas that are now Cecil clay. Naturally this feature tends to accentuate the higher clay levels in the South.

In figures 2 and 3 all points which represent soils of the clay types (Cecil clay) have been marked by a little dash, and, indeed, many of the higher clay values *appear* to be related to sheet erosion. To test further the quantitative influence of erosion, table 8 containing the data of table 7 split into two groups according to textural differences,[2] has been constructed: first, the heavy-textured soil types (clays and clay loams), which supposedly owe their clayey

TABLE 8

Data showing that the clay content increases in light-textured as well as in heavy-textured soils

Glaciated areas excluded

GROUPS	TEMPERATURE INTERVAL, 10–13°C.		TEMPERATURE INTERVAL, 16–19°C.		INCREASE
	Samples	Clay	Samples	Clay	
		per cent		*per cent*	*per cent*
Light textures only	33	22.0 ±1.20	20	32.9 ±1.30	50
Heavy textures only	7	30.8 ±2.33	13	43.4 ±1.75	41

TABLE 9

The clay content of subsoils of light- and heavy-textured soils as related to temperature intervals

Glaciated areas excluded

GROUPS	TEMPERATURE INTERVAL, 10–13°C.		TEMPERATURE INTERVAL, 13–19°C.		INCREASE
	Samples	Clay	Samples	Clay	
		per cent		*per cent*	*per cent*
All textures	40	24.8 ±1.32	33	44.8 ±1.42	81
Light textures only	33	23.2 ±1.22	20	41.7 ±1.65	80
Heavy textures only	7	32.8 ±2.96	13	49.7 ±1.96	52

surface layer to erosion; and, secondly, the light-textured soils, which represent more nearly the original conditions. According to table 8 both groups are characterized by specific clay levels. The most important feature lies in the consistency of the higher clay levels in the South as compared with the North.

The factor erosion can be practically eliminated by restricting the comparisons to the clay content of the subsoil or B-horizon. This has been done in table 9. The latitude effect is even more strikingly manifested than in the profile data of table 8. The subsoil clay levels change from 24.8 per cent to

[2] According to the United States Soil Survey the texture of a soil type is determined upon the mechanical analyses of only the surface soil.

44.8 per cent clay, the increase amounting to over 80 per cent. The difference, 20.0 ±1.95 per cent, is highly significant. Again the north-south correlation holds for coarse-textured as well as fine-textured soils. Particular significance should be attached to the fact that within each temperature class the heavier soil types tend to have more clay in the subsoil than the lighter types. Apparently the higher clay content of eroded soil profiles (e.g., clays and clay loams of table 8) is not entirely due to the exposure of the subsoil but is primarily a consequence of the inherently higher clay content of the entire profile. It is quite possible that these different values of the two texture groups reflect differences in the degree of maturity of the soils.

The data in tables 8 and 9 strongly suggest that erosion plays but a minor rôle in the clay latitude relationship, and in the following discussions it is considered as negligible.

Discussion of the moisture influence

The seasonal variations of precipitation, which are similar over the entire area, belong to the so-called Eastern Rainfall Type, which is characterized by a comparatively uniform distribution of rainfall throughout the year. In the northern region a fraction (less than one fifth) of the annual precipitation falls as snow, which "affords the water better facilities for soaking into the ground than though the same amount was poured down during the comparatively brief period of a shower" (7).

The average annual rainfall for the temperature class 10–13°C. is 48.0 ±1.35 inches, and the corresponding value for the 16–19°C. class is 48.9 ±0.43 inches. Inasmuch, as this difference is insignificant one might be tempted to consider the graphs of figures 2 and 3 and the data in tables 6–9 as the clay temperature functions searched for. Such a procedure can not be correct because it neglects the rôle of temperature in increasing transpiration and evaporation. Crowther (3) has shown that under conditions of Rothamsted lysimeters, temperature markedly influences the amount of water percolating through the soil. To maintain constant drainage a temperature rise of 1°F. must be accompanied by 0.75 inches more rain. When *Crowther's leaching factor* was calculated for all counties, satisfactory clay-temperature relations were obtained. However, for the sake of comparison with previous work and with studies on other continents the N.S. Quotient, which is closely related to the precipitation-evaporation ratio, was chosen as the moisture criterion (4).

The clay moisture function

According to the data in table 4, there exists between moisture values and temperature a negative correlation, which can be expressed mathematically as

$$\text{N.S.Q.} = -20.6\,T + 6.55 \quad (r = -0.680) \qquad (E)$$

$$\text{Leaching factor} = -1.03\,T + 53.0 \quad (r = -0.534) \qquad (F)$$

These correlations state that with increasing temperature the effective moisture values become smaller. On the basis of the selected moisture criteria there is actually less effective moisture in the South than in the North and the specific rôle of temperature is overshadowed. To discover the true influence of temperature, evaluation of the clay-moisture functions is required.

In a previous publication (5) it was demonstrated that, for soils from homogeneous as well as heterogeneous parent materials, at a constant temperature of 12°C. (11.1–13.3°), the clay content of the soil varies with N.S.Q. as follows:

$$\text{per cent clay} = m\ (\text{N.S.Q.}) + n \qquad (G)$$

where m and n are constants. Equation (G) can be applied with little difficulty to crystalline rocks. For instance, for the series "granite, gneiss, and schists," the average clay content at 12°C. (11.1–13.3°) is 25.6 per cent and N.S.Q. is 400 (table 4). The ratio 25.6:400 yields the constant m in equation (G). For crystalline rocks in general the constant n can be taken as zero, hence

$$\text{per cent clay} = 0.064\ \text{N.S.Q.}_{(T\,=\,12)} \qquad (H)$$

which represents the clay-moisture relation for the parent material group (g).

The final clay-temperature functions

It is reasonable to assume that equation (G) is not only valid at 12°C. but also at other temperatures, and on this basis it is possible to calculate the clay levels for any desired N.S.Q. value. In order to remain within the humid region all data have been adjusted to N.S.Q. = 400 by use of the equation:

$$\text{Per cent clay}_{400} = \text{clay}_{N.S.Q.} \times \frac{400}{\text{N.S.Q.}} \qquad (I)$$

where clay $_{\text{N.S.Q.}}$ and N.S.Q. are the observed corresponding values in tables 1–4. Several typical curves are shown in figures 4–7 and the data can all be represented by the general equation:

$$\text{Log}_{10}\ \text{per cent clay} = aT_{0°}^{20°} + b, \text{ or,} \qquad (J)$$

after transformation to natural logarithms,

$$\text{per cent clay} = Ce^{kT_{0°}^{20°}} \qquad (K)$$

Table 10 contains the values of the constants a and b, and also the correlation coefficients of equation (J) for all groups of parent materials investigated. Since all correlations are significant, the conclusions follow that the *clay content of comparable soils increases exponentially with increasing temperature.*

Many other equations might fit the data equally well as, if not better than, equation (J). It is simply claimed that equation (J) is able to describe the

relationships significantly as judged by statistical criteria. The reason for avoiding straight line functions, as might be suggested by figures 5 and 6, is

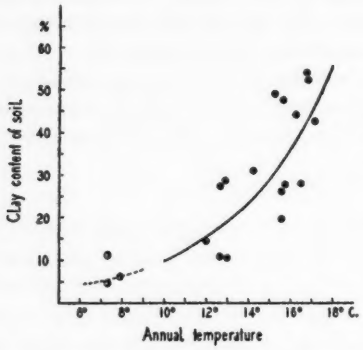


FIG. 4. CLAY-TEMPERATURE FUNCTION FOR THE PARENT MATERIAL GROUP (a) "GRANITES"

Data adjusted to constant N.S.Q. 400. Semi-black points refer to glaciated regions, e.g., soils developed on granitic moraines.

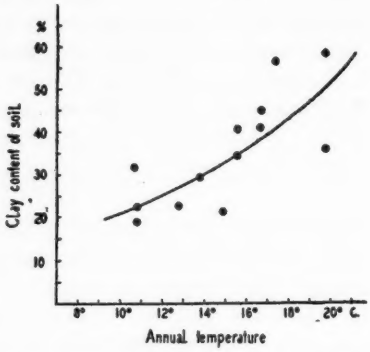


FIG. 5. CLAY-TEMPERATURE FUNCTION FOR THE PARENT MATERIAL GROUP (b) "GNEISSES"

Data adjusted to constant N.S.Q. 400.

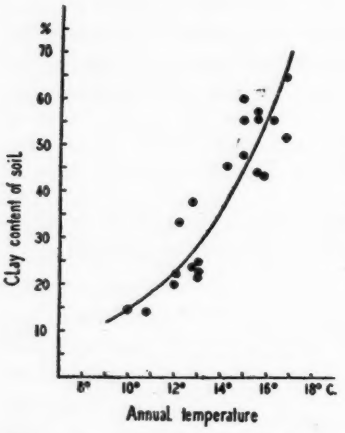


FIG. 6. CLAY-TEMPERATURE FUNCTION FOR THE PARENT MATERIAL GROUP (d) "BASIC ROCKS"

Data adjusted to constant N.S.Q. 400.

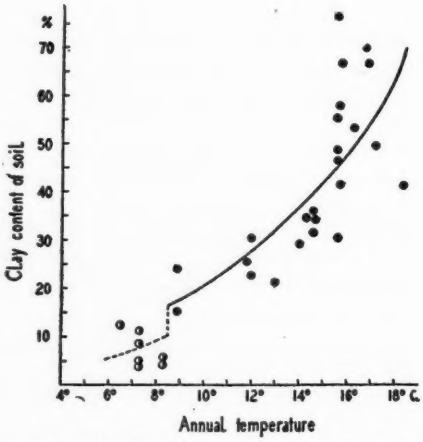


FIG. 7. CLAY-TEMPERATURE FUNCTION FOR THE PARENT MATERIAL GROUP (g) "GRANITES, GNEISSES AND SCHISTS"

Semi-black points refer to soils derived from moraines.

that absurd extrapolations at lower temperatures would result, for instance 0 per cent clay at 8°C. for figure 6. At annual temperatures higher than 20°C.,

equation (J) is probably no longer justified because the clay content of a soil can not exceed 100 per cent. Above 20°C. the partial differential coefficient $\frac{\partial\,(\text{clay})}{\partial(\text{temp})}$ tends to become zero and some sort of an S-shaped curve is to be expected.

Relation to Van't Hoff's law

On thermodynamic grounds, Van't Hoff (8) has suggested that the velocity constant of a chemical reaction depends on temperature probably as follows:

$$\frac{d\,ln\,k}{dT} = \frac{A}{T^2} + B \qquad (L)$$

where k is the velocity constant and A and B are functions of temperature. This is Van't Hoff's law, or what he, himself, called "the fundamental equation." In order to render it suitable for practical purposes it must be integrated, and in this manipulation considerable arbitrariness enters. As a first approach Van't Hoff treats A and B as constants and observes experimental agreement by putting either A or B equal to zero. In the first case one obtains

TABLE 10

Clay-temperature relation for N.S.Q. = 400

Equation (J) (Unglaciated region only)

NUMBER	PARENT MATERIAL	NUMBER OF PROFILES	a	b	CORRELATION COEFFICIENT r
a	Granites	16	0.0961	0.020	+0.737
b	Gneisses	13	0.0388	0.939	+0.760
c	Schists	17	0.0376	1.028	+0.595
d	Basic rocks	21	0.100	0.147	+0.918
e	Granites and gneisses	24	0.0606	0.658	+0.559
f	Gneisses and schists	17	0.0422	0.955	+0.497
g	Granites, gneisses, and schists	24	0.0622	0.686	+0.824

$$\frac{d\,ln\,k_1}{dT} = B$$

which gives by integration

$$ln\,k_1 = BT \times c$$

or

$$k_1 = c_1 e^{BT} \qquad (M)$$

This is known as Berthelot's equation. It indicates that the reaction velocity increases exponentially with rise in temperature. In the second case, by setting $B = 0$, one finds

$$\frac{d\,ln\,k_2}{dT} = \frac{A}{T^2}$$

or integrated

$$ln\,k_2 = -\frac{A}{T} + c$$

or

$$k_2 = c_2 e^{-\frac{A}{T}} \qquad (N)$$

This form also leads to an exponential velocity temperature relation.

It is certain that A, which includes the heat of reaction, is not a constant, but nearly so for temperatures which are not too far apart, say, T_1 and T_2. For such a temperature interval Van't Hoff's law takes the form:

$$ln\frac{k_{T_2}}{k_{T_1}} = A\int_{T_1}^{T_2}\frac{dT}{T^2} = -A\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

or

$$k_{T_2} = k_{T_1} e^{A\left(\frac{T_2 - T_1}{T_1 T_2}\right)} \qquad (O)$$

This particular equation is known as Arrhenius' temperature law (1). Again the velocity increases exponentially with rising temperature.

Though Van't Hoff's fundamental equation applies only to reactions in which the equilibrium constant (k) has a definite meaning, it has been found that many irreversible and living processes exhibit a similar trend between speed of transformation and temperature. In particular it has been observed that in numerous systems *a temperature rise of 10°C. increases the reaction velocity two to three times, a relationship known as Van't Hoff's temperature rule.*

It is evident that the clay-temperature curves obtained resemble Van't Hoff's exponential functions. At higher temperatures the clay content of the soil does not increase merely in proportion to temperature, but much more rapidly. As for Van't Hoff's 10°C. rule, this is obeyed strictly in only three cases (curves b, c, f, table 11) giving quotients 2–3; in two systems (curves e, g) the quotient is about 4, which is not an uncommon value, whereas for the curves (a) and (d) the ratios are very high, namely, 9 and 10.

If the soils south of the glaciated area are considered to be of similar age, the differences in their average clay content will reflect the variations in the velocity of clay accumulation. In accordance with Van't Hoff's law one would

have to conclude that the process of rock decomposition and clay formation is the more rapid the higher the temperature.

A search through the literature reveals that the data presented appear to be the first numerical and statistical proof that the clay content of soils and consequently the profile texture vary with climate, particularly temperature. Many soil scientists have tacitly assumed such a relationship, but several authorities have voiced different opinions. Merrill (7) says, "For many years an impression has prevailed to the effect that rocks decomposed more rapidly in warm and moist than in cold climates . . . such has not yet been proven to actually take place, and indeed many facts tend to prove the impression quite erroneous." Marbut (6) states, "There is no harmonious relationship between soil texture and the environment in which the textures occur. They occur in a wholly hit or miss way in any kind of geographic environment."

Upon a critical survey of the data at hand the author has not been able to

TABLE 11

Velocity of clay formation as related to Van't Hoff's temperature rule

10°C. interval from 8–18°C.

NUMBER	PARENT MATERIAL	AVERAGE CLAY CONTENT ON THE BASIS OF EQUATION (*J*)		RATIO $\frac{\text{CLAY (18°C.)}}{\text{CLAY (8°C.)}}$
		At 8°C.	At 18°C.	
		per cent	*per cent*	
c	Schists	21.3	50.7	2.4
b	Gneisses	17.7	43.4	2.5
f	Gneisses and schists	19.6	51.9	2.7
e	Granites and gneisses	13.9	56.1	4.0
g	Granites, gneisses, and schists	15.3	63.9	4.2
a	Granites	6.2	56.2	9.1
d	Basic rocks	8.8	88.5	10.0

find a more satisfactory explanation of the clay-latitude correlation than that furnished by the causal rôle of temperature.

The idealized clay-climate surface

After evaluation of the separate effects of moisture and temperature on clay formation it becomes possible to establish an idealized clay-climate equation which contains both climatic variables and which is of the general form.

$$\Gamma = f(H, T) \qquad (P)$$

where Γ represents the average clay content of the soil in per cent, H the annual moisture value (N.S.Q.), and T the annual temperature in degrees centigrade. Equation (P) can be written in differential notation as follows:

$$d\Gamma = \left(\frac{\partial \Gamma}{\partial H}\right)_T dH + \left(\frac{\partial \Gamma}{\partial T}\right)_H dT \qquad (Q)$$

The partial differential coefficient $(\partial\Gamma/\partial H)_T$ can be determined with the aid of the clay moisture correlation (H)

$$\Gamma = mH,$$

or

$$\left(\frac{\partial\Gamma}{\partial H}\right)_T = \frac{\Gamma}{H} \qquad (R)$$

The partial differential coefficient $(\partial\Gamma/\partial T)_H$ follows from equation (K) and is

$$\left(\frac{\partial\Gamma}{\partial T}\right)_H = k\Gamma \qquad (S)$$

Inserting equations (R) and (S) into equation (Q) one obtains for Γ under the assumption that the constants are independent of climate the following

$$\int \frac{d\Gamma}{\Gamma} = \int \frac{dH}{H} + k \int dT, \qquad (T)$$

or

$$\Gamma = cHe^{kT} \qquad (U)$$

where c and k are constants. On account of the empirical nature of the surface, H should not be extended over 400, and T should be restricted to the interval 5–20°C.

In order to arrive at specific values for c and k we shall choose the data of the parent material group (e) "granites and gneisses" as given in table 10. The value of c is found to be 0.014 and that of $k = 0.140$, (0.0606 x 2.30). Equation (U) becomes

$$\text{Per cent clay} = \Gamma = 0.0114He^{0.140T} \qquad (V)$$

and its graph is shown in Figure 8.

The meaning of this clay-climate surface can be stated as follows:

Figure 8 illustrates the relation between clay content of soil and temperature and moisture, in absence of disturbing conditions (absence of glaciation, constancy of other soil forming factors). It applies only to residual soils derived from mixtures of granites and gneisses. In other words, if the entire United States were covered by granites and gneisses the graph would show the variation of the climatic clay content of the soils formed. Naturally the surface is an abstraction and as such not exactly true to nature, but it proves itself of great value in visualizing the distribution of climatic clay and the fluctuations of soil texture under a given set of conditions. In particular, figure 8 yields the following information:

Under conditions of limited moisture the clay content of the soil is very low, regardless of the temperature.

With increasing moisture the clay content increases in proportion to N.S.Q.[3] The rate of increase is greatest in the South and smallest in the North.

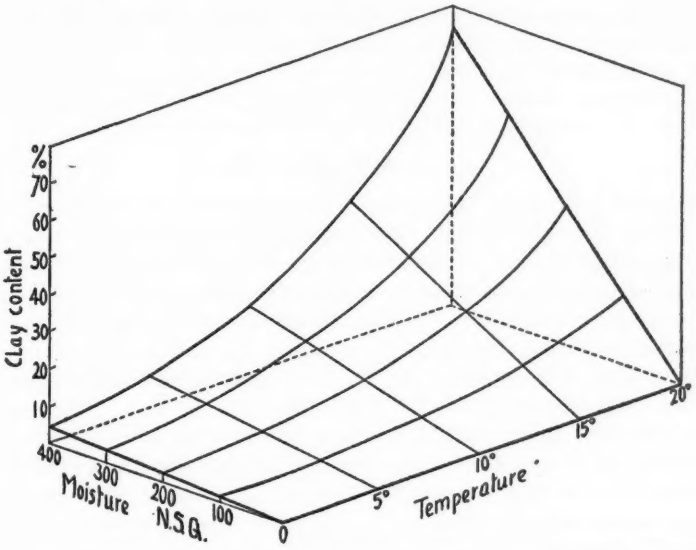


FIG. 8. IDEALIZED CLAY-CLIMATE SURFACE, SHOWING THE VARIATION OF "CLIMATIC CLAY" IN SOILS DERIVED FROM GRANITES AND GNEISSES AS A FUNCTION OF MOISTURE AND TEMPERATURE

TABLE 12

Clay content (0–40-inch depth) of idealized soils derived from granites and gneisses for selected moisture and temperature values. Constancy of other soil forming factors assumed

	°C.	INCREASING MOISTURE (N.S.Q.) ⟶			
		N.S.Q.			
		100	200	300	400
Increasing temperature ↓	0°	1.1% clay	2.3% clay	3.4% clay	4.6% clay
	5°	2.3% clay	4.6% clay	6.9% clay	9.2% clay
	10°	4.6% clay	9.2% clay	13.9% clay	18.5% clay
	15°	9.3% clay	18.6% clay	27.9% clay	37.2% clay
	20°	18.8% clay	37.5% clay	56.3% clay	(75.0)% clay

With increasing temperature the clay content of the soil increases exponentially. The effect of temperature is most pronounced in the humid region and the least in the arid. Southern soils contain more clay than northern ones (compare table 12).

[3] It is likely that in the subtropics and tropics the function $\Gamma = f$ (moisture) is not merely a straight line but of logarithmic type [compare reference (5)].

A comparison of the clay-climate surface with the nitrogen-climate function published previously (4) is of interest. In regard to *moisture*, the effect is similar in both instances, namely, an increase in nitrogen and clay with higher N.S.Q. figures. On the other hand, *temperature* has an opposite influence on the two outstanding soil properties. It tends to accumulate clay but lowers the nitrogen and organic matter content. In other words, for the systems under consideration, northern soils are rich in organic matter and poor in clay (climatic), whereas southern soils possess much clay but little organic matter.

SUMMARY

The clay contents of 151 soil profiles developed on crystalline rocks in the eastern United States were correlated with climatic factors.

It was observed that within each of seven different groups of parent materials the average clay content of the soil increases from north to south.

Temperature is considered to be the major factor that is responsible for the high clay levels in the South.

For constant moisture values the clay-temperature function is of exponential nature and resembles Van't Hoff's temperature rule.

An idealized clay-climate surface has been constructed which shows the variation of "climatic clay" in soils derived from granites and gneisses as a function of moisture and temperature.

REFERENCES

(1) ARRHENIUS, S. 1889 Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren. *Ztschr. Phys. Chem.* 4: 226–234.

(2) Bureau of Chemistry and Soils, U. S. Dept. Agr. 1900–1930 Field Operations (Reports and Maps).

(3) CROWTHER, E. M. 1930 The relationship of climatic and geological factors to the composition of soil clay and the distribution of soil types. *Proc. Roy. Soc.* [London] *Ser.* B. 107, 30 pp.

(4) JENNY, H. 1930 A study on the influence of climate upon the nitrogen and organic matter content of the soil. Missouri Agr. Exp. Sta. Res. Bul. 152.

(5) JENNY, H., AND LEONARD, C. D. 1934 Functional relations between soil properties and rainfall. *Soil Sci.* 38: 363–381.

(6) MARBUT, C. F. 1928 A scheme for soil classification. *Proc. First Internatl. Cong. Soil Sci.* 4: 1–31.

(7) MERRILL, G. P. 1906 Rocks, Rock-weathering and Soils. New York.

(8) VAN'T HOFF, J. H. 1884 Etudes de Dynamique Chimique. Amsterdam.

SORPTION OF PHOSPHATES BY NON-CALCAREOUS HAWAIIAN SOILS

L. E. DAVIS[1]

Experiment Station, Hawaiian Sugar Planters' Association

Received for publication September 18, 1934

An investigation of the chemistry of "phosphate fixation" in Hawaiian sugar cane soils has been pursued primarily with the hope that a contribution to practical agriculture would ensue. In the course of this study sufficient experimental evidence has been obtained to justify the formulation of a tentative theory of this phenomenon.

The pronounced tendency of Hawaiian soils to "fix" applied phosphates was investigated by Crawley (3) as early as 1902, later by McGeorge (10) and more recently by Hance (7) and Ayres (1).

Historical discussions and rather extensive bibliographies have been made available by Weiser (21) and Williams (22). Only such papers as appear immediately pertinent to the discussion will be cited here.

The expression "phosphate fixation," although apparently somewhat crude, is very useful, since no preconception of a mechanism is involved. Since the present study is of a purely chemical nature, it becomes convenient to restrict the expression to measurable chemical relationships. Phosphate fixation is taken to imply the following phenomenon: When a solution of orthophosphates is applied to soil, there is a decrease in the concentration of phosphates in the solution. No considerations of availability of the fixed phosphate to plants are involved in this convention.

A priori, four principal ways in which this decrease in concentration might occur are suggested:

I. Cations of soluble salts present in the soil or cations replaced from the soil by those present in the solution form precipitates with the phosphate ions. II. By double decomposition, relatively insoluble soil minerals react to form insoluble phosphates. III. Phosphates are adsorbed at the extensive soil-solution interface. IV. Phosphates are absorbed by the soil minerals to form complex systems in one or more of the solid soil phases.

It is extremely probable that several reactions take place in any soil when phosphates are applied. It is interesting to discover evidence pointing to dominance of one of these types.

In recent years most writers have concluded that phosphate fixation is

[1] The writer wishes to express his appreciation of the advice and criticism of Dr. Francis E. Hance, under whose direction this study was pursued, and of Arthur Ayres and P. L. Gow.

largely due to the formation of insoluble precipitates, rather than to sorption. Following Comber (2) and Fisher (5) the opinion has generally been accepted that Russell and Prescott (18) were in error when they ascribed their results to adsorption. More recently Ford (6), Dean (4), and others have presented evidence which can be interpreted as indicating the formation of complex addition compounds.

EXPERIMENTAL STUDIES

Most upland Hawaiian soils are lateritic, with a high content of hydrated iron oxides, a low silica-sesquioxide ratio, a relatively high content of titanium, a moderate supply of magnesium, a low content of calcium, and a moderately acid reaction. Phosphate fixation is very pronounced; in some cases there is little or no crop response to moderate applications of phosphatic fertilizers, but a response to rather large applications.

Results from experiments with two soils of high fixing capacity are discussed in this paper. [Other similar materials have been less extensively studied, particularly by Ayres (1), with consistent results.]

Soil No. 7582—A dark brown surface soil from upper Manoa Valley, on the Island of Oahu.

Soil No. 7512—A yellowish brown subsoil from the northeastern part of the Island of Kauai.

Air-dried, pulverized materials were continuously agitated (usually in an end-over-end tumbler) with solutions of phosphates. Clear filtrates were obtained either by gravity filtration through Whatman No. 12 folded filter paper, by rapid suction through Whatman No. 42 paper, or by filtration under 100 pounds pressure through Chamberland-Pasteur Filter Cylinders No. 7. In the latter case sufficient solution was discarded to allow for the sorption by the cylinder.

In most of the experiments rather high concentrations were employed. The solutions and filtrates were analyzed by the official methods for solutions of fertilizers (A.O.A.C. II). For phosphates the volumetric method was used, for potash the Lindo-Gladding method. pH values were determined either colorimetrically with a LaMotte Roulette Comparator or, when necessary, by a glass electrode. A few exceptions will be noted in the context of each experiment.

The following abbreviations are employed in the tables and figures:

P_I = initial concentration of P in the solution
P_E = concentration of P after agitation of the solution with soil
ΔP = change in concentration.
Corresponding symbols are used for K and H.

The data are expressed as millimols of solute per liter of solution.

Rate of fixation

A 200-gm. portion of air-dried soil No. 7582, passed through a 1-mm. mesh sieve, was agitated with 2 liters of a solution containing 5.0 gm. P_2O_5 as a mixture of $(NH_4)H_2PO_4$ and $(NH_4)_2HPO_4$, 20 gm. of NH_4Cl, 20 cc. formalin solution, and enough NH_4OH to bring the pH to 6.8. Small samples of the mixture were removed and rapidly filtered at intervals. The filtrates were then analyzed. The results are presented in table 1. At the end of 16 days the phosphate concentration of the solution had been greatly diminished. Apparently appreciable, but not very large, amounts were still being fixed.

TABLE 1

Rate of fixation of phosphates

200 gm. soil no. 7582, 2000 cc. solution, pH = 6.8

TIME	P_E	ΔP
Ammonium phosphate and ammonium chloride solutions P_I = 35.20 millimols per liter		
days		
3	4.08	31.12
7	2.18	33.02
11	1.68	33.52
16	1.34	33.86
After addition of extra phosphate P_I = 29.92 millimols per liter		
1	24.22	5.70
7	17.60	12.32
14	15.50	14.42
28	11.48	18.44
49	8.94	20.98
85	6.65	23.27

A concentrated solution of ammonium phosphate was then added. After the solution was shaken to effect thorough mixing, a sample was removed and rapidly filtered. The concentration then determined was arbitrarily taken as a new value of P_I. The mixture was then agitated for 85 days longer with occasional samplings as before. It is evident that at these new concentrations considerably more phosphate was fixed, and that the rate was increased, although it was not nearly so great as the initial rate of the first series. The rate of fixation at any moment is, as one would expect, a function of the concentration in the solution and the amount already fixed by the soil.

A series of separate portions of soil No. 7512 was intermittently agitated with a potassium phosphate solution to which HCl had been added until the

pH was 0.25. The flasks were removed at intervals, the mixtures filtered, and the solutions analyzed. The data are presented in table 2. The pH values are also given. These results will be referred to later in another connection. A continuous agitation of soil No. 7512 (pulverized, and passed through an 80-mesh sieve) with solutions of high and low initial concentrations of phosphate at a pH of 7.0 showed that final equilibrium can be reached in 15 days with continuous mixing.

Although the initial rate of fixation is large, the process does not proceed rapidly to its termination. This condition is quite consistent with the idea that fixation is due to double decomposition or to absorption, but most particularly with the idea that it is due to the latter. It is probably, not necessarily, inconsistent with the hypothesis that fixation is due to precipitation by replaced

TABLE 2

Rate of fixation of phosphoric acid

10 gm. soil no. 7512, 100 cc. solution. $pH_I = 0.25$. $P_I = 49.5$ millimols per liter
Potassium phosphate solutions with added HCl

TIME	pH_E	P_E	ΔP
1.5 hrs.	0.25	37.5	12.0
3	0.25	36.0	13.5
6	0.25	33.7	15.8
1 day	0.30	30.6	18.9
2	0.50	28.0	21.5
3	0.58	27.2	22.3
4	0.56	26.1	23.4
5	0.58	25.3	24.2
7	0.70	23.9	25.6
9	0.70	22.9	26.6
11	0.70	22.9	26.6
12	0.70	23.2	26.3
14	0.70	22.3	27.2
16	0.70	22.0	27.5
18	0.70	21.7	27.8

bases. A permutite saturated with Ca^{++} was agitated with potassium phosphate solutions at a pH of 9.6. It had been previously determined that the sodium compound fixed only very small amounts of phosphorus at this pH. In 2 days a state of equilibrium had been attained. This experiment is by no means conclusive since the conditions of exchange in soils may be different from those in the artificial material and an adhering precipitate of calcium phosphate may impede the progress of further exchange in the soil much more than in the permutite.

The very slow attainment of equilibrium in the system implies that other processes than adsorption play a large part in fixation of phosphates, since adsorption equilibria are usually rapidly reached.

The formal characteristics of equilibria between soil and phosphate solutions

Portions of finely pulverized soil No. 7512 were continucusly agitated with solutions prepared from KH_2PO_4, K_2HPO_4, and formalin. The period of mixing was 22 days. It is believed, from the results of an experiment described in the foregoing, that a final equilibrium was reached in that time. Four different amounts of soil were used with the same volume of solution. In each of these four series the phosphate concentration was varied. The pH of the solutions was not quite the same in all cases, because of the effect of dilution, but approximated an average of 7.0 for the group. It was impracticable to run the agitations in duplicate, but all analyses were checked by a reëxamination of the filtrates at a separate time. The averages of closely agreeing results

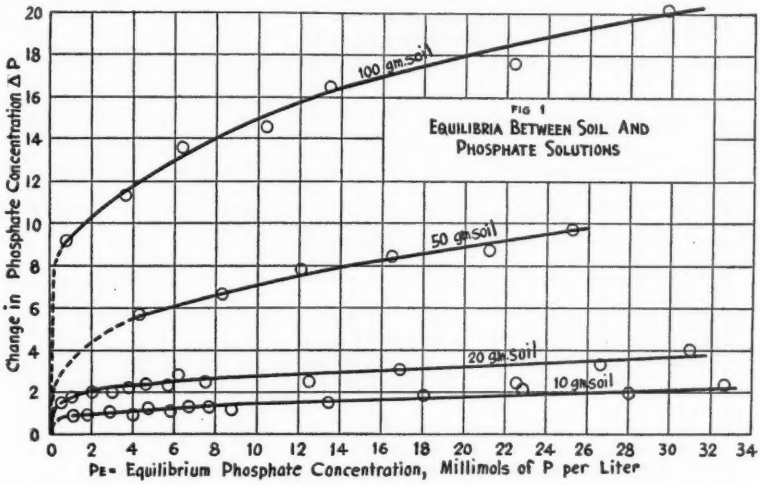


FIG 1
EQUILIBRIA BETWEEN SOIL AND PHOSPHATE SOLUTIONS
100 gm. soil
50 gm. soil
20 gm. soil
10 gm. soil
Change in Phosphate Concentration ΔP
Pe= Equilibrium Phosphate Concentration, Millimols of P per Liter
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34
0 2 4 6 8 10 12 14 16 18 20

FIG. 1

are presented in table 3 and the function $\Delta P = F(P_E)$ is plotted in figure 1. The corresponding logarithmic function is plotted in figure 2 for two of the series. The solutions were prepared from a standardized stock solution, and several dilutions were checked by analysis. For this reason the values of P_I are correctly presented in round numbers. With a fairly high degree of approximation, the curves can be expressed empirically by the function $\Delta P = kP_E^{1/3}$, which is Freundlich's adsorption isotherm. On the basis of these curves phosphate fixation could easily be ascribed, as has been done by Russell and Prescott (18), to adsorption by the soil colloids. Fisher (5) has shown that the existence of such curves is not a sufficient criterion and has also stated that chemical precipitations could yield similar curves. Langmuir (8) has shown that adsorptions do not always give a curve of this form. One must certainly agree that since more than one process probably occurs during fixation, too

much stress should not be laid upon the precise form of the curve. Nevertheless, this stricture does not constitute proof that the process is not adsorption; it merely implies the need of corroborative evidence.

Curves of this general form might be expected from theoretical considerations in the case of a number of hypothetical reactions. In all cases the discussion can be simplified by neglecting the increase in concentration which may be due to sorption of pure water.

Let us assume first that calcium present in the base exchange complex precipitates phosphates. Take the simple reaction:

$$(A) \qquad K_2HPO_4 + CaZ_2 \leftrightarrow 2KZ + CaHPO_4.$$

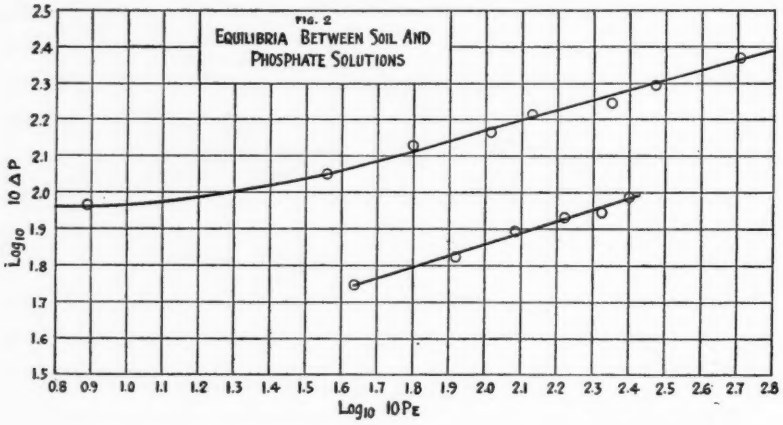


FIG. 2

In the following discussion the theory of Vanselow (20) is accepted. He has presented evidence to show that the various substances present in the base exchange complex (symbolized as CaZ_2, KZ, etc.) probably exist in the complex as mixed crystals and that the activity of each can be considered equal to its mol fraction. If we assume further that the activity of K_2HPO_4 is proportional to its concentration in the solution we can express the equilibrium as follows:

$$(B) \qquad k = \frac{\left[\frac{KZ}{CaZ_2 + KZ}\right]^2}{(K_2HPO_4)\left[\frac{CaZ_2}{CaZ_2 + KZ}\right]}$$

In any single experiment the initial number of mols of base exchange complex is a constant, i.e.,

$$z = CaZ_2 + \frac{KZ}{2}, \text{ constant.}$$

Also $P_E = (K_2HPO_4)$, and the change in concentration, ΔP, is equal to the number of mols of $CaHPO_4$ formed per unit volume of solution, which is again equal to one-half the number of mols of KZ formed per unit volume of solution, i.e., when V = volume of the solution; $\Delta P = \frac{KZ}{2V}$, and $CaZ_2 = z - V\Delta P$, and $CaZ_2 + KZ = z + V\Delta P$.

Then

$$(C) \qquad k = \frac{4V^2\Delta P^2}{P_E(z - V\Delta P)(z + V\Delta P)}$$

and

$$(D) \qquad \Delta P = \frac{z}{V}\sqrt{\frac{kP_E}{4 + kP_E}}$$

If kP_E is very small compared with 4, the expression assumes very approximately the form $\Delta P = k' P_E^{1/2}$.

In any event we can show that the curve should be concave downwards with a steep slope at the origin and a slope approaching zero at the upper limb.

Taking the derivative, we have

$$(E) \qquad \frac{d\Delta P}{dP_E} = \frac{2zk^{1/2}}{VP_E^{1/2}(4 + kP_E)^{3/2}},$$

from which

$$(F) \qquad \frac{d\Delta P}{dP_{E_{P_E=0}}} = \infty$$

Also:

$$(G) \qquad \frac{d^2\Delta P}{dP_E^2} = -\frac{4zk^{1/2}}{V}\left[\frac{kP_E + 1}{P_E^{3/2}(4 + kP_E)^{5/2}}\right]$$

Setting the second derivative equal to zero, we get: $P_E = 1/k$. The only point of inflection is at a negative value of P_E; it therefore has no physical significance. We can see from the negative sign of the second derivative that the curve is concave downward throughout its positive branch.

The preceding discussion was based on the assumption that the activity of K_2HPO_4 is proportional to its concentration, an assumption that will be approximately correct for low concentrations, but not necessarily for high concentrations. Thus it is clear that near the origin the slope will be very great, but it is not certain that we are justified in assuming that the derivation

$$\frac{d\Delta P}{dP_{E_{P_E=\infty}}} = 0, \text{ is physically correct.}$$

However, from general consideration we can derive this result. When P_E is greatly increased, ΔP cannot increase without limit, since its value must

approach as a limit z or some lesser quantity. Accordingly $\frac{d\Delta P}{dP_E}$ must approach zero.

From equation (*D*) we see that for any given value of P_E, the ordinate on the curve, ΔP varies as the ratio z/V, i.e., as the ratio between the amount of soil and solution. In the curves of figures 1 and 2, this relationship is shown to exist.

If next we consider a possible double decomposition reaction:

$$(H) \qquad 2PO_4^{\equiv} + 3CaCO_3 \leftrightarrow Ca_3(PO_4)_2 + 3CO_3^{=},$$

then for small concentrations,

$$(I) \qquad k = \frac{(CO_3)^3}{(PO_4)^2}$$

$$P_E = PO_4^{\equiv}, \Delta P = \frac{CO_3^{=}}{3}$$

or

$$(J) \qquad \Delta P = \frac{k^{1/3} P_E^{2/3}}{3}$$

and finally

$$(K) \qquad \frac{d\Delta P}{dP_E} = \frac{2k^{1/3}}{9P_E^{1/3}},$$

and

$$(L) \qquad \frac{d\Delta P}{dP_{E_{P_E=0}}} = \infty$$

It cannot be shown quite rigorously that, as P_E increases greatly, the slope approaches zero, since we do not know how the concentrations vary with the activities. It is exceedingly probable that the curve is concave downward throughout its course, since the second derivative has a negative value:

$$(M) \qquad \frac{d^2\Delta P}{dP_E^2} = -\frac{2k^{1/3}}{27P_E^{4/3}},$$

which holds for points close to the origin.

For any given value of P_E, the ordinate ΔP is independent of the mass of the solid reactant (in this case $CaCO_3$). We should not expect then a series of curves when we vary the ratio of soil to solution, but rather a single curve, the length of which would depend upon the amount of solid present. That is to say, obviously if all the solid is destroyed the curve must terminate.

We find here a very serious objection to the hypothesis that phosphate fixation is largely due to a double decomposition. The situation is by no

means saved by assuming that a number of such reactions occur, since the relative amounts would not be changed by altering the absolute quantities. If at any point one of the solids should be totally consumed, we should get at most a discontinuity in the curve, and not a series of curves.

Finally, let us consider the case of an absorption. It is presumed that a portion of the soil material is of such a character that solutes can penetrate to a slight extent and will be distributed between this material as one phase and the liquid solution as another phase. This hypothesis resembled Vanselow's (20) theory of base exchange. However, in base exchange, from the point of view of the amount of base held by the soil, there is no real significance to the concept of equilibrium between the substrate Z^-, and the bases (including H^+), since in order to have electrical neutrality the substrate must be saturated. The reactions consist not of reactions between substrate and bases but of exchange of bases. The differential equilibria are presumably due to the different activities of the bases and to different degrees of dissociation of the salts formed. In the development of his theory Vanselow has apparently neglected the effect of Donnan equilibria. For the moment a discussion of such effects will be omitted from the following absorption theory.

In the case of phosphate absorption we shall assume, on the contrary, that a reaction occurs between the soil substrate and the phosphate to form new complex compounds. The amounts of these compounds formed will depend upon the activities of the various reactants. It will be convenient to discuss the equilibria due to diffusion of one phosphate ion or compound and reaction with one soil substrate.

If P_E equals the concentration of a phosphate in the liquid phase, then as long as the activity is proportional to the concentration we can write that the activity is equal to tP_E. At equilibrium the activities of the phosphate in the two phases must be proportional, according to Henry's law. If P_s equals the activity of the phosphate in the solid phase, then $tP_E = sP_s$, and we can reduce this to $P_s = hP_E$.

Let us take the case of a reaction between the phosphate in the solid phase and a component of that phase:

$$(N) \qquad P + B \leftrightarrow PB$$

Let P_r equal the activity of PB, and B_s the activity of B. Then:

$$(O) \qquad k = \frac{P_r}{P_s \cdot B_s} = \frac{P_r}{hP_E \cdot B_s}$$

Assume that the activities of all components are equal to their mol fractions in the reactive solid phase. Let N equal the total number of mols of all substances present, and b the initial number of mols of B. Then P_rN, P_sN, B_sN, will equal the number of mols of PB, P and B, respectively, present in the solid phase. Also $B_sN = b - P_rN$ and,

$$(P) \qquad k = \frac{P_r}{hP_E \dfrac{(b - P_rN)}{N}} = \frac{P_rN}{hP_E(b - P_rN)}.$$

Then

$$(Q) \qquad P_rN = \frac{kbhP_E}{1 + khP_E}$$

Now the total number of mols of the phosphate which have left the solution equals the total number of mols of phosphate which are present in the soil phase at equilibrium. Let V equal the volume of the solution, which we shall assume has not changed during the reaction. Then

$$(R) \qquad V\Delta P = P_sN + P_rN$$

Substituting $P_s = hP_E$ and (Q), we have

$$(S) \qquad \Delta P = \frac{1}{V}\left[hP_EN + \frac{kbhP_E}{1 + khP_E}\right]$$

Now N is a variable. Let Q be the number of mols of any substances not taking part in the reaction, e.g., H_2O, then

$$N = P_sN + B_sN + P_rN + Q$$
$$N = P_sN + b - P_rN + P_rN + Q$$

or

$$(T) \qquad N = \frac{b + Q}{1 - P_s} = \frac{b + Q}{1 - hP_E}$$

Then substituting (T) in (S), we have

$$(U) \qquad \Delta P = \frac{hP_E}{V}\left[\frac{b + Q}{1 - hP_E} + \frac{kb}{1 + khP_E}\right]$$

Now from our knowledge of the very small absorption of chlorides, sulfates, etc. [*see* Mattson (13)] it is reasonable to suppose that the amount of free phosphate in the solid phases is small also. That is, hP_E is small compared with unity. The magnitude of h will depend, of course, upon the unit (mols or millimols, etc.) used for P_E. For simplicity, let us assume that Q is small compared with b. Then we get

$$(V) \qquad \Delta P = \frac{hP_Eb}{V}\left[1 + \frac{k}{1 + khP_E}\right], \text{ approximately.}$$

Further, if we suppose, in accordance with experimental results, that ΔP is of about the magnitude of P_E, i.e., $10^{-1} < \dfrac{\Delta P}{P_E} < 10$, we can say that also

$$10^{-1} < \frac{hb}{V}\left[1 + \frac{k}{1 + khP_E}\right] < 10.$$

From similar considerations of the amount of soil used per liter of solution we can say that b/V is of about the magnitude of P_E. Then $\frac{hb}{V}$ must, like hP_E, be very small, and $\left(1 + \frac{k}{1 + khP_E}\right)$ must be rather large. Therefore $\frac{k}{1 + khP_E}$ is large compared with unity, and we can reduce the expression further to:

$$(W) \qquad \Delta P = \frac{\frac{kbhP_E}{V}}{1 + khP_E} = \frac{k_2P_E}{1 + k_1P_E}, \text{ approximately.}$$

This expression has the form of Langmuir's adsorption formula (8).

Taking the derivative of (U) we have

$$(X) \qquad \frac{d\Delta P}{dP_E} = \frac{h}{V}\left[\frac{b + Q}{(1 - hP_E)^2} + \frac{kb}{(1 + khP_E)^2}\right].$$

This can also be reduced to the form

$$(Y) \qquad \frac{d\Delta P}{dP_E} = \frac{hb}{V}\left[1 + \frac{k}{(1 + khP_E)^2}\right]$$

and when P_E is very small, the slope approaches the value:

$$(Z) \qquad \frac{d\Delta P}{dP_{E_{P_E=0}}} = \frac{hb(1 + k)}{V}$$

As P_E increases in value, hP_E still being very small as compared with unity, we approach a range where khP_E becomes large compared with unity and we then have:

$$(AA) \qquad \frac{d\Delta P}{dP_E} = \frac{b}{VkhP_E^2}, \text{ approximately.}$$

But since, as we have seen, $\frac{k}{1 + khP_E}$ is large compared with unity, k must be large also and as P_E becomes large the derivative becomes small or

$$(BB) \qquad \text{limit } \frac{d\Delta P}{dP_E} = 0.$$

The curve may have a steep slope at the origin, the slope decreasing as the curve is ascended. The logarithmic curve is not linear, as may be shown by taking the logarithm of both sides of (U), giving

$$(CC) \qquad \log \Delta P = \log \frac{h}{V} + \log P_E + \log \left[\frac{b+Q}{1-hP_E} + \frac{kb}{1+khP_E} \right]$$

$$(DD) \qquad \frac{d \log \Delta P}{d \log P_E} = 1 + hP_E \left[\frac{\dfrac{b+Q}{(1-hP_E)^2} - \dfrac{k^2 b}{(1+khP_E)^2}}{\dfrac{b+Q}{1-hP_E} + \dfrac{kb}{1+khP_E}} \right].$$

Again this may be reduced, when hP_E is small, to the form:

$$(EE) \qquad \frac{d \log \Delta P}{d \log P_E} = 1 - \frac{khP_E}{1+khP_E} = \frac{1}{1+khP_E}$$

The slope varies between unity and zero, but Langmuir (8) has shown that just this type of curve can be obtained for adsorption of gases. Thus it is quite possible that an absorption would yield curves similar to those obtained from adsorption.

It will be noted from equation (V) that when ΔP is plotted as a function of P_E, the ordinates will be proportional to b/V, that is, to the ratio between the amount of soil used and the volume of solution. We have a family of curves with b/V as a variable parameter.

Since there are possibly present in a natural soil replaceable bases which can precipitate phosphates, as well as more than one absorbent, an interface for adsorption, and more than one phosphate ion, $H_2PO_4^-$, $HPO_4^=$, etc., we should in general expect more than one reaction to be possible.

Consider an idealized experiment: A definite amount of a single soil absorbent is treated with a series of solutions of different concentrations, and a curve is drawn. An additional constant amount of soil reactant and sufficient phosphate is now added to each mixture so that the former equilibrium concentration P_E is reached The increase in the ordinates will be proportional to the increase in soil reactant, and the resultant curve belongs to the same family as the first curve, with b as the variable parameter. If now we had added a different soil reactant, the constants k, h, etc. would have becomes variable also and the resultant curve would generally have had a different analytical form from the original curve. Thus it is possible that the actual experimental curves obtained will not correspond to those characteristic of any single reaction.

To sum up: The form of a single fixation curve experimentally obtained does not certainly imply any particular type of reaction nor necessarily exclude any. The existence of a series of curves for different ratios of soil to solution shows definitely that double decomposition plays a minor part in fixation.

In passing, a few arguments for and against the adsorption hypothesis may

well be discussed. It is known that whereas phosphates are strongly fixed by soils, sulfates and chlorides are not. In soil No. 7582 the sorption of chloride ion was found to follow a very nearly linear function between concentrations of 5 millimols and 5,000 millimols per liter. The percentage sorption was about 3.5, whereas the fixation of phosphates varied from over 80 per cent at $P_E = 50$ millimols per liter to 99.8 per cent at very small concentrations. This difference is sometimes supposed to be due to the fact that phosphoric acid is tribasic, apparently as the result of a confusion with the well-known fact that the discharging power of ions is a function of their valence. At any rate there is certainly very little trivalent ion present in neutral or acid solutions. Mattson (13) has found that ferrocyanides are not strongly fixed by soil. On the other hand it is objected occasionally that soil colloids are negatively charged and therefore will not adsorb anions. This objection would be pertinent if we considered only electrolytic replacement (polar adsorption). But it is by no means certain that phosphates are not strongly held by non-polar adsorption.

Reversal of fixation equilibria by dilution of the mixtures

A pertinent objection to assigning adsorption a dominant rôle in fixation of phosphates is the rather slow rate of such fixation contrasted to the rapid rate of most reactions which are well established as adsorptions. It was observed, however, that mixtures of soil and phosphate solutions became more and more difficult to filter and remained as suspensions longer, as the process of mixing progressed. It was thought possible that, because of progressive dispersion, fresh surface was continuously presented for adsorption.

Alongside the series shown in table 3, in which 50 gm. of soil was agitated with 1 liter of solution, another series was run in which 50 gm. of soil and 500 cc. of solutions, with double the concentration in each case, were shaken for the same time. At the end of this period 500 cc. of water was added to each of the latter series, and the bottles were again shaken for 4 hours. Thus finally the same amount of soil, water, and phosphorous was present in the corresponding members of each series.

The data are presented in table 4 and the results are plotted in figure 3. The columns and curve marked "A" were obtained by interpolation from the curve of the series in which 100 gm. of soil was shaken with 1,000 cc. of solution (*see* figure 1), since this ratio is equal to that for 50 gm. of soil and 500 cc. of solution. The values of $P_E/2$ and $\Delta P/2$ are calculated. This curve then represents the concentrations which should exist immediately upon dilution with 500 cc. of water. The columns and curve "B" represent the data for an agitation of 50 gm. of soil and 1,000 cc. of solution (*see* figure 1). This is, of course, the ideal for completely reversed equilibria of the series A. The columns and curve "C" represent the actual situation after 4 hours of agitation of the diluted solution.

The equilibria were reversed, but only to a certain extent. Considerations of progressive dispersion do not enter here, and one must suppose that adsorp-

TABLE 3

Equilibria between soil and phosphate solution

Soil no. 7512, pH_I = approximately 7.0. Agitation continuous for 22 days
Potassium phosphate solutions, 1000 cc.

P_I	10 GM. SOIL		20 GM. SOIL		50 GM. SOIL		100 GM. SOIL	
	P_E	ΔP	P_E	ΔP	P_E	ΔP	P_E	ΔP
2.00	1.07	0.93	0.54	1.46				
2.75	1.76	0.99	1.01	1.74				
4.00	2.89	1.11	2.00	2.00				
5.00	4.04	0.96	2.96	2.04				
6.00	4.74	1.26	3.78	2.22				
7.00	5.83	1.17	4.61	2.39				
8.00	6.71	1.29	5.67	2.33				
9.00	7.70	1.30	6.17	2.84				
10.00	8.80	1.20	7.46	2.54	4.32	5.68	0.78	9.22
15.00	13.48	1.52	12.48	2.52	8.30	6.70	3.65	11.35
20.00	18.13	1.87	16.87	3.13	12.14	7.86	6.35	13.65
25.00	22.91	2.09	22.56	2.44	16.52	8.48	10.41	14.59
30.00	28.04	1.96	26.65	3.35	21.24	8.76	13.50	16.50
35.00	32.65	2.35	30.96	4.04	25.24	9.76		
40.00							22.37	17.63
50.00							29.77	20.23
75.00							51.52	23.48

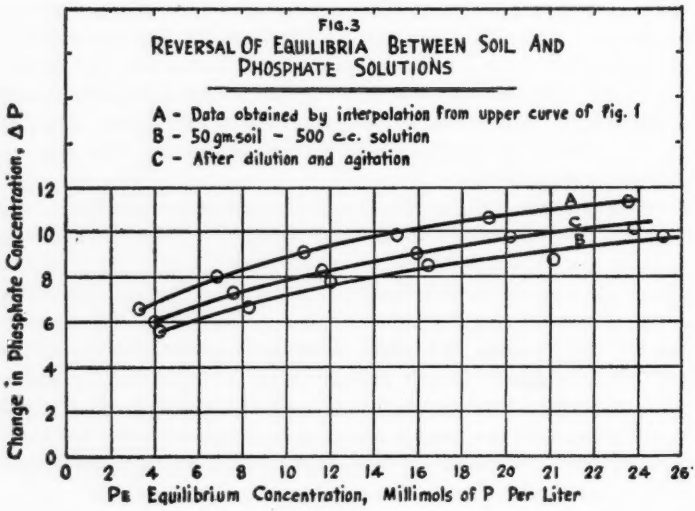


FIG. 3

tion would have been more nearly reversed in 4 hours. It is suggested that we have either reversed an absorption or partially redissolved precipitates formed earlier. Dean (4) has recently shown that phosphorous fixed in soils with a high content of hydrated iron oxides are, like the phosphates of dufrenite (a basic ferric phosphate), only rather slowly removed by electrodialysis. One would expect more rapid removal of phosphates if they had been adsorbed.

TABLE 4

Reversal of fixation equilibria

Soil no. 7512, $pH_I = 7.0$

A		B		C	
$P_E/2$	$\Delta P/2$	P_E	ΔP	P_E	ΔP
3.38	6.62	4.32	5.68	4.04	5.96
6.90	8.10	8.30	6.70	7.65	7.35
10.85	9.15	12.14	7.86	11.69	8.31
15.10	9.90	16.52	8.48	15.96	9.04
19.32	10.63	21.24	8.76	20.24	9.76
23.60	11.40	25.24	9.76	23.87	11.13

A. Results obtained by interpolation from last two columns of table 3—50 gm. soil—500 cc. solution.

B. Results obtained as in table 3 with 50 gm. of soil and 1,000 cc. of solution.

C. Results obtained after dilution of 50 gm. soil and 500 cc. of solution followed by agitation for 4 hours.

Fixation by soil from which the easily replaced bases have been exchanged for ammonium and potassium ions

Ammonium ions were substituted for the other bases in the base exchange complex of soil No. 7582 by percolation. Four specimens were prepared as follows:

I. Five liters of NH_4OH solution—1–10—were percolated through 100 gm. of soil. This was followed by a solution containing 10 gm. NH_4Cl per liter, acidified slightly with HCl, and later by a solution containing 10 gm. NH_4Cl per liter at a pH of 7.0 until the percolate had a pH of 7.0.

II. Ten liters of 1 per cent NH_4Cl solution at pH = 7.0 were percolated through 100 gm. of soil until the pH of the percolate was 7.0.

III. A percolation with 5 liters of 0.5 *N* HCl was followed by one with a solution of NH_4OH and NH_4Cl until the pH of the percolate was 7.0.

IV. One hundred grams of soil was brought to moisture saturation with 1 per cent NH_4Cl solution.

A liter of ammonium phosphate solution at pH 7.0, containing 49.3 millimols of P per liter was added to each of the moist specimens. The mixtures were agitated for 60 hours and were then filtered through filter paper. The results are presented in table 5.

The acid treatment removed considerable amounts of aluminum and iron,

as well as calcium and magnesium; the NH_4OH treatment removed small amounts of aluminum and a great quantity of organic matter.

It appears that the replaceable bases account for only a small fraction, 3.7 per cent, of the phosphate fixed under these conditions.

Bases present in filtrates after fixation of phosphate

Four 100-gm. samples of soil No. 7582 were agitated for 24 hours with 1,000 cc. of ammonium phosphate solutions at pH 7.0, containing 10 gm. NH_4Cl. In general this ratio of soil to solution was used in the experiments which are discussed hereinafter. Phosphorus, silica, and certain bases were determined by Paul Chu. The results are presented in table 6.

TABLE 5

Phosphate fixed by soils treated to exchange NH_4^+ and H^+ for other bases

100 gm. soil 7582, 1000 cc. solutions. $pH_I = 7.0$. $P_I = 49.3$ millimols per liter

PREVIOUS TREATMENT	P_E	ΔP
NH_4OH, NH_4Cl	18.6	30.7
NH_4Cl	15.4	33.9
HCl, NH_4Cl	27.3	22.0
No percolation	14.1	35.2

TABLE 6

Composition of filtrate after agitation of soil and phosphate solutions

100 gm. soil 7582, 1000 cc. solutions (quantities in millimols per liter)

P_I	P_E	ΔP	SiO_2	Ca	Mg	Mn	Al	Fe	Ti
0	0	0	0.12	0.94	1.64	0.26	Trace	Trace	None
5.63	0.03	5.60	0.25	0.91	1.60	0.13	Trace	Trace	None
14.10	0.40	13.70	0.45	0.77	1.46	0.07	Trace	Trace	None
70.40	27.10	43.33	1.33	0.05	0.49	0.02	None	Trace	None

We see clearly that precipitates of calcium, magnesium, manganese, and aluminum phosphates have been formed wherever the phosphate concentration was high enough to exceed the solubility products of the various compounds. It is of interest to note that silica is removed by the higher concentrations of phosphates.

Fixation of basic ions accompanying phosphate ions

Portions of soil No. 7582 were agitated for 48 hours with solutions of potassium chloride, ammonium chloride, potassium phosphate, and ammonium phosphate. The bases as well as the phosphate were determined and the results are presented in table 7. The last four treatments in the table were agitated for 24 hours instead of 48 hours.

After these results had been obtained all the solutious and filtrates from the final equilibrium experiment obtained with soil No. 7512 (*see* table 3) were analyzed for potassium. The results are presented in table 8 and plotted in figure 4. It was found that the potash equilbria were reversed like the phosphate equilibria and to about the same extent.

Portions of soil No. 7582 were shaken for 48 hours with a series of ammonium phosphate solutions at pH 6.8 which contained also 10 gm. NH_4Cl per liter. Both P and NH_4[2] were determined (table 9).

TABLE 7

Fixation of basic ions

Soil no. 7582

SALT	pH_I	P_I	P_E	ΔP	K_I OR $(NH_4)_I$	K_E OR $(NH_4)_E$	ΔK OR ΔNH_4
KCl	6.8				85.1	75.6	9.5
NH_4Cl	6.8				75.3	70.5	4.8
KH_2PO_4, K_2HPO_4	6.8	50.0	16.3	33.7	78.5	32.9	45.6
$(NH_4)H_2PO_4$, HCl	4.0	47.9	12.9	35.0	48.0	21.1	26.9
KH_2PO_4, K_2HPO_4	6.8	52.4	22.0	30.4	78.4	45.1	33.3
KH_2PO_4, HCl	4.0	52.4	13.4	39.4	78.4	55.7	22.7
$(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$	6.8	52.6	22.0	30.6	73.5	41.6	31.9
$(NH_4)H_2PO_4$, HCl	4.0	52.6	15.4	37.2	73.5	48.0	25.5

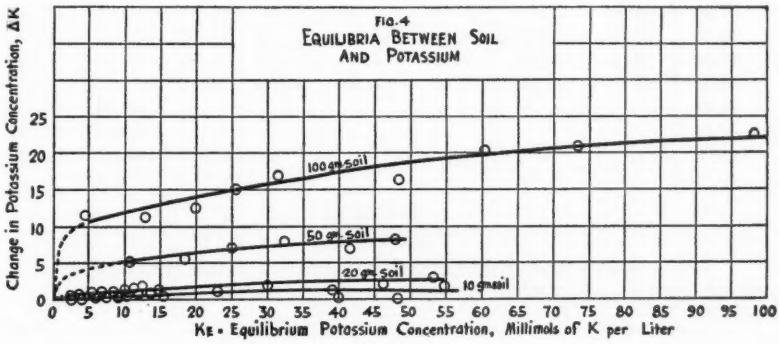


FIG. 4
EQUILIBRIA BETWEEN SOIL AND POTASSIUM
100 gm. soil
50 gm. soil
20 gm. soil
10 gm. soil
Change in Potassium Concentration, ΔK
0 5 10 15 20 25
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100
KE = Equilibrium Potassium Concentration, Millimols of K per Liter

FIG. 4

It is very evident that in the process of fixation of phosphates basic ions are also fixed to a great extent. The amounts of bases (exclusive of H) fixed are roughly proportional to the amounts of phosphate fixed. The relative amounts would depend, of course, upon the amounts of H fixed and would thus vary with the pH of the solutions, as will be shown later. It is significant that where an additional salt was present more of the base was fixed.

[2] The author is indebted to Q. H. Yuen for the determinations of ammonium ion.

The ratio of base to H is greater. The phenomenon is analogous to base exchange.

Soil No. 7582 was treated by percolation in duplicate with the following solutions:

I. 4 liters 0.001 *N* HCl
II. 2.5 liters 1.0 KCl
III. 2.5 liters 1.0 *N* $CaCl_2$

TABLE 8

Equilibria between soil and potassium in potassium phosphate solutions

Soil no. 7512, pH_I = appxorimately 7.0. 1,000 cc. of solutions

10 GM. SOIL			20 GM. SOIL		50 GM. SOIL		100 GM. SOIL	
K_I	K_E	ΔK	K_E	ΔK	K_E	ΔK	K_E	ΔK
3.22	2.95	0.27	2.76	0.46				
4.43	4.18	0.25	3.72	0.71				
6.45	5.89	0.56	5.46	0.99				
8.06	7.38	0.68	6.89	1.17				
9.67	8.96	0.71	8.50	1.17				
11.28	10.52	0.76	9.85	1.43				
12.90	12.19	0.71	11.35	1.55				
14.50	13.74	0.76	12.58	1.92				
16.10	15.50	0.60	14.75	1.35	10.75	5.35	4.44	11.66
24.18	22.94	1.24	22.82	1.36	18.50	5.68	12.81	11.37
32.24	30.59	1.65	30.08	2.16	25.00	7.24	19.83	12.41
40.30	39.95	0.35	39.17	1.13	32.40	7.90	25.63	14.94
48.36	48.38	−0.02	46.28	2.08	41.50	6.86	31.36	17.00
56.42	54.75	1.67	53.32	3.10	48.00	8.42		
64.48							48.30	16.18
80.60							60.31	20.29
120.90							98.32	22.58

TABLE 9

Fixation of bases

Soil no. 7582, $(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$, + 1 per cent NH_4Cl

P_I	P_E	ΔP	NH_{4I}	NH_{4E}	ΔNH_4
5.63	0.01	5.62	191.2	172.4	18.8
14.08	0.16	13.92	205.6	175.7	29.9
42.24	6.76	35.48	268.0	204.3	63.7
70.40	23.30	47.10	324.7	233.1	91.6

The pH of each solution was adjusted so that in the case of the KCl and $CaCl_2$ percolations the final portions of the percolate had a pH of 7.0. No calcium was found in the last portions of percolates I and II. The materials were then repeatedly washed with 95 per cent ethyl alcohol until the washings were free from chlorides. A washing with ethyl ether was then followed by

drying with a current of air. The residues were then agitated for 24 hours with potassium phosphate solutions at a pH of 7.0. The results are given in table 10.

These results show conclusively that potassium phosphate is fixed by a sorption process in this soil. In the last case the additional fixation due to the precipitation of calcium phosphate is clearly shown. It is of interest to note that possibly slightly more phosphate was fixed in the soil which had been treated with acid than in that treated with KCl. Also more potash was fixed by the soil treated with HCl than by that treated with $CaCl_2$. It is suggested that the strongly buffered potassium phosphate solution is capable of replacing almost all the H^+ in the base exchange complex, as well as almost all of the calcium, the latter effect due to removal of Ca^{++} to form precipitates. Then if somewhat more phosphate is fixed by an acid soil than by a neutral soil we should expect somewhat more potassium to be fixed also.

TABLE 10

Fixation of phosphate and potassium by materials in which H^+, K^+ and Ca^{++} had replaced other bases

Soil no. 7582, experiments in duplicate. $P_I = 49.06$. $K_I = 78.21$

TREATMENT	P_E	ΔP	K_E	ΔK
HCl	29.64	19.42	53.32	24.89
HCl	29.99	19.07	53.48	24.73
KCl	30.69	18.37	61.46	16.75
KCl	30.34	18.72	61.46	16.75
$CaCl_2$	25.69	23.37	54.55	23.66
$CaCl_2$	25.98	23.08	54.39	23.82

Fixation from solutions of different hydrogen-ion concentrations

A series of potassium phosphate solutions was prepared and adjusted to various pH values by the addition of HCl or KOH, and of KCl, in such a way as to maintain the same concentration of K and P throughout the series.

Both the soils No. 7582 and 7512 were shaken with these solutions for 72 hours. The pH values were determined with a glass electrode. The results are presented in tables 11, 12, and 13. The data in table 13 were obtained at another time, and unfortunately the period of agitation was only 24 hours instead of 72. For this reason the results do not coincide. Also ΔK and ΔH were not determined. The calculation of ΔH from pH values becomes less accurate in this range. The values of ΔH are the sums of the changes in H-ion concentration plus the hydrogen absorbed as $HPO_4^=$ etc. These quantities have been calculated from the initial and final pH values, and the initial and final concentrations of P by the use of a graph (prepared by P. L. Gow) in which the mol fractions of H_3PO_4, etc., are plotted as functions of the pH.

TABLE 11

Fixation of phosphate, potassium, and hydrogen from solutions of different pH values

Soil no. 7582, P_I = 50.00 millimols per liter. K_I = 96.84 millimols per liter

pH_I	pH_E	P_E	ΔP	K_E	ΔK	ΔH	$\frac{\Delta H + \Delta K}{\Delta P}$
2.03	4.32	6.35	43.65	78.08	18.76	122.4	3.23
3.01	5.45	12.34	37.66	68.87	27.97	84.1	2.97
4.05	5.70	13.65	36.35	66.23	30.61	75.4	2.90
5.02	5.79	13.91	36.09	66.32	30.52	73.0	2.87
6.04	6.87	14.96	35.04	62.37	34.47	70.5	3.00
7.04	7.60	20.26	29.74	59.57	37.27	43.9	2.74
8.03	8.23	23.65	26.35	56.94	39.90	28.1	2.62
9.00	8.50	24.26	25.74	53.73	43.11	25.3	2.67

TABLE 12

Fixation of phosphate, potassium, and hydrogen from solutions of different pH values

Soil no. 7512, P_I = 50.00 millimols per liter. K_I = 96.84 millimols per liter

pH_I	pH_E	P_E	ΔP	K_E	ΔK	ΔH	$\frac{\Delta H + \Delta K}{\Delta P}$
2.03	3.20	18.44	31.56	92.57	4.27	96.3	3.18
3.01	5.45	28.18	21.82	86.39	10.45	64.5	3.44
4.05	5.70	29.39	20.61	84.42	12.42	45.9	2.83
5.02	5.83	29.56	20.44	85.41	11.43	44.0	2.72
6.04	6.75	30.78	19.30	84.83	12.01	47.2	3.08
7.04	7.85	33.39	16.61	82.03	14.81	30.7	2.74
8.03	8.35	35.57	14.43	79.65	17.19	16.1	2.31
9.00	8.90	36.26	13.74	78.58	18.26	13.8	2.34

TABLE 13

Fixation of phosphates at various low pH values

P_I = 50.00 millimols per liter

pH_I	SOIL NO. 7582			SOIL NO. 7512		
	pH_E	P_E	ΔP	pH_E	P_E	ΔP
3.03	5.45	17.0	33.0	5.28	31.8	18.2
2.72	5.23	15.5	34.5	4.88	31.1	18.9
2.46	4.97	11.1	38.9	4.38	28.9	21.1
2.15	4.59	10.9	39.1	3.45	25.1	24.9
1.95	4.17	8.8	41.2	2.93	22.5	27.5
1.81	3.75	5.6	44.4	2.58	21.3	28.7
1.59	2.83	3.0	47.1	2.20	20.9	29.1
1.41	2.51	4.1	45.9	2.02	22.2	27.8
1.21	2.36	7.7	42.3	1.82	23.5	26.5

The relation between phosphate fixed and the final pH is plotted in figure 5, and the graph is presented as figure 6.

As might be expected on the basis of a sorption theory, the relative amounts

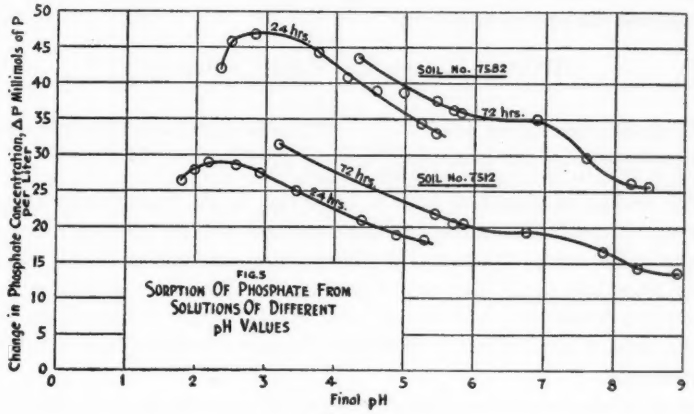


FIG. 5

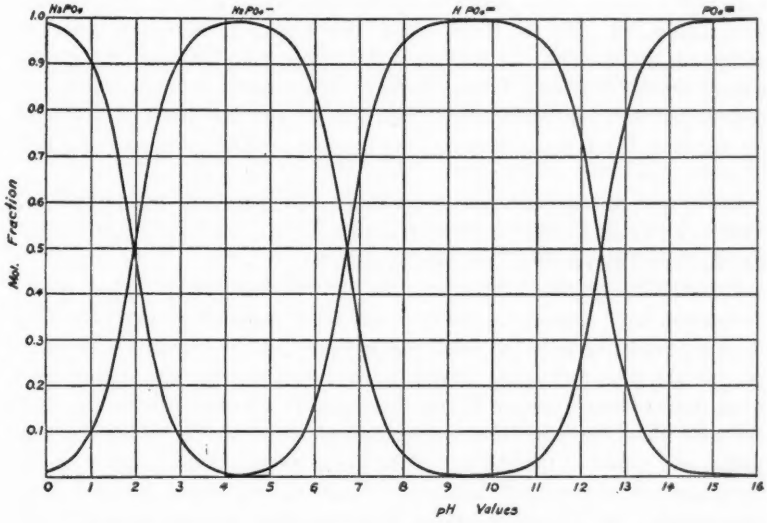


FIG. 6. MOL FRACTIONS OF PHOSPHORIC ACID AND ITS IONS AT VARIOUS pH VALUES

of ΔH and ΔK vary inversely, and the ratio $\frac{\Delta H + \Delta K}{\Delta P}$ is approximately equal to 3. The possible accumulation of errors in this ratio (due to analysis and calculation) must be very great. Furthermore, the existence of side reactions

involving exchange of H^+ and K^+ for undetermined cations and those involving the solution of organic matter by the more alkaline solutions would affect this value. In particular, the solution of organic acids would increase the hydrogen present in the solution without altering the concentration of potassium. We can express this process as follows:

(*FF*) $$HPO_4^{=} + \text{H-Humate} \leftrightarrow H_2PO_4^{-} + \text{Humate}^{-}.$$

We should then expect that $\frac{\Delta H + \Delta K}{\Delta P}$ would be decreased in alkaline media, which is seen to be the case in tables 11 and 12.

The amount of phosphate fixed is a function of the hydrogen-ion concentration. This situation would be quite consistent with an adsorption hypothesis, as was shown by Mattson (16), who, however, varied both the pH and the initial phosphate concentrations of his solutions. It is also consistent with an absorption hypothesis, if we assume different absorption constants for each of the series of ions. There is, however, another plausible explanation of this phenomenon.

In the discussion of the absorption hypothesis it was assumed that phosphates would be distributed between the solid and liquid phases in accordance with Henry's Law. This might be approximately true if the new compounds were not ionized. But the theory should be extended for the case where these complexes are ionized. In that case the Donnan equilibria might greatly change the distribution. Furthermore, if the complexes are amphoteric, the distribution would depend upon the pH, according to the principles developed by Mattson (15) in his discussion of the Donnan equilibrium in an amphoteric colloid.

Let us first consider the cases in an acid media, where we should have immobile cations surrounded by mobile anions, in this case $H_2PO_4^-$ and $HPO_4^{=}$ and at lower pH values by undissociated H_3PO_4.

I. Following Mattson (15), let z be the "concentration" (the concept "concentration," instead of activity or mol fraction is loosely used here, since we are considering only the relative magnitudes of the amounts of $H_2PO_4^-$, etc., in the solid and liquid phases, respectively, and are not attempting a quantitative formulation) of $H_2PO_4^-$ belonging to the immobile cations inside the solid phase, let y be the concentration of "free" $H_2PO_4^-$ inside the solid phase, and x that of the $H_2PO_4^-$ in the liquid phase. Then y and x are the concentrations of the mobile cation, K^+, inside and outside of the solid phase, respectively. In the concentrated KH_2PO_4 solutions employed in these experiments we may neglect H^+ in comparison with K for pH values above 3.

(*GG*) $$\text{Then } \underset{H_2PO_4^-}{x \text{ (outside)}} \; \underset{K^+}{x \text{ (outside)}} = \underset{K^+}{y \text{ (inside)}} \; \underset{H_2PO_4^-}{(y + z) \text{ (inside)}}$$

and

(*HH*) $$x^2 = y(y + z)$$

then

(*II*) $$x < y + z$$

or

(*JJ*) $$\underset{\text{outside}}{H_2PO_4^-} < \underset{\text{inside}}{H_2PO_4^-}$$

II. Let z be the concentration of $HPO_4^=$ belonging to the immobile cations, let y and x be the free $HPO_4^=$ inside and outside, respectively, then $2y$ and $2x$ are the corresponding concentrations of K. Then

(*KK*) $$4x^3 = 4y^2(y + z)$$

and

(*LL*) $$x < y + z$$

or

(*MM*) $$\underset{\text{outside}}{HPO_4^=} < \underset{\text{inside.}}{HPO_4^=}$$

III. Undissociated H_3PO_4 will not be affected by the Donnan equilibria. Accordingly, after a certain point, as the pH is lowered and the ratio $H_2PO_4^-/H_3PO_4$ decreases, we should expect the ratio between phosphate inside and that outside to decrease also.

Let us now consider three cases which might occur in alkaline solutions where we should expect imobile anions.

IV. Let z equal the concentration of K^+ belonging to the immobile anions, y that of $H_2PO_4^-$ (neglecting OH^- which will be small where appreciable amounts of H_2PO_4 are present) inside, and x that outside y and x also represent free K inside and outside. Then

(*NN*) $$x^2 = y(y + z)$$

and

(*OO*) $$x > y$$

or

(*PP*) $$\underset{\text{outside}}{H_2PO_4^-} > \underset{\text{inside}}{H_2PO_4^-}$$

V. Let z have the same meaning as in case (IV), let y and x refer to $HPO_4^=$ inside and outside. Then $2y$ and $2x$ refer to free K^+.

Then

$$(QQ) \qquad 4x^3 = y(2y + z)^2$$

and

$$(RR) \qquad x > y$$

or

$$(SS) \qquad \underset{\text{outside}}{HPO_4^{=}} > \underset{\text{inside}}{HPO_4^{=}}$$

VI. Considering the case of $PO_4^{\equiv}$ ions we have, since $K = 3y$, etc.

$$(TT) \qquad 27x^4 = y(3y + z)^3$$

$$(UU) \qquad x > y$$

or

$$(VV) \qquad \underset{\text{outside}}{PO_4^{\equiv}} > \underset{\text{inside}}{PO_4}$$

At very high pH values, the concentrations of OH^- will become appreciable; therefore, for a rigorous presentation, they should be included. The expression, however, becomes complicated. The presence of OH^- will diminish slightly the tendency for phosphate to be excluded from the solid phase. At the isoelectric point we should expect a simpler distribution corresponding to Henry's Law.

Then considering alone the distribution as we proceed from very low to higher pH values, we should expect first an increase in the phosphate absorbed, then a maximum, then a decrease, and finally a continued decrease at a slower rate. But the amount of phosphate complex and therefore the concentration of z is a function of y. Let us assume that we have brought a system of soil and phosphate solution to equilibrium at the isoelectric point. Now, if we acidify the solution we increase the concentration of phosphate ions present in the solid phases, but this also increases the amount of complex formed. Inverse considerations apply to a solution made alkaline. The effects due to the Donnan equilibrium are magnified and we should expect a fairly steep curve with a point of inflection at the isoelectric point, which need not necessarily be the same as the isoelectric point for the soil as a colloidal system.[3]

All these considerations are exhibited in the experimental curves in figure 5. The apparent point of inflection in each curve at pH = 6.5 approximately may possibly be due to experimental errors. An extended investigation of sorption by a series of soils at different acidities is now under way, and this point, among others, will be then cleared up. The maxima between pH 2 and 4 most probably are augmented by the considerable amount of iron which would go

[3] In the development of this theory the author is indebted to P. L. Gow for his advice and assistance.

into solution and which would precipitate phosphates. For this reason it is questionable to attempt to obtain a final equilibrium in such a range of pH values. The results obtained are to be considered as indicative of what ideally could be expected at final equilibrium if, unfortunately, the acids did not break up the soil material to some extent. Probably it is approximately correct to assume that at any moment during the process of an absorption we have a true equilibrium set up with respect to the depth to which the various ions have penetrated the solid phases, if the reactions are rapid compared to the rate of diffusion.

Midgley (17) has found that Na_2HPO_4 is much less readily fixed than K_2HPO_4. If we assume that the more greatly hydrated ions are less firmly held than those less strongly hydrated, that is that the dissociation of a phosphate complex compound follows the lyotropic series for cations, it is possible to explain this phenomenon. In other words the hypothetical sodium phosphate complex is assumed to be more highly dissociated than the corresponding potassium complex. Thus we should expect the Donnan equilibrium effect to be very pronounced. On the other hand, Lohse and Ruhnke (9) found apparently that even NaH_2PO_4 was less strongly fixed than KH_2PO_4. However, they were investigating, not equilibria, but the amounts of phosphate extracted by a $KHSO_4$ solution in 5 minutes of shaking. The soil treated with NaH_2PO_4 was possibly more highly dispersed than that treated with KH_2PO_4. This, taken in conjunction with the fact that the soil was allowed to dry out in contact with the salt solutions instead of being agitated, which would prevent a very deep-seated absorption, would possibly result in a more rapid reversal of the fixation in one case than in another. The author has under way equilibrium experiments in which potassium and sodium phosphates are to be absorbed by sodium and potassium saturated soils under acid and alkaline conditions.

Sorption of phosphates from very acid solutions

Both of the soils 7582 and 7512 were agitated with very acid phosphate solutions. In an earlier experiment soil No. 7582 was treated with solutions of varying strengths of phosphoric acid for a period of 24 hours. The exact initial and final pH values were not determined. Nevertheless the final pH was probably below 1.0, as judged by the succeeding experiments. The results are presented in table 14.

Samples of both the soils were agitated in a series of flasks with portions of a very acid solution. These flasks were removed from the agitator from time to time. The filtrates were analyzed for phosphates, and the initial and final pH values were determined by the glass electrode. The results for the soil No. 7512 have been presented in table 2.

Of the elements commonly present in soils only one, titanium, could form precipitates in so acid a solution. The solubility of the phosphates of Fe, Al, Ca, and Mg is too great to permit the assumption that they could have been

precipitated, at least with the concentrations of H_3PO_4 present. For the sake of completeness this fact was verified by a few simple experiments. A titanium sulfate solution at a pH of 0.45 was added to a phosphate solution at the same pH. Upon shaking, a copious precipitate appeared. It was found that the TiO_2 content of soil No. 7512 was 9.6 per cent. It therefore seemed possible that the fixation of phosphates in this acid media might be due to precipitation of a titanium phosphate.

However, extraction of this soil with an HCl solution maintained at about pH = 0.5 yielded only a trace of titanium. No precipitate is formed when a

TABLE 14

Fixation of Phosphates from solutions at pH values below 1.0

Soil no. 7582

P_I	P_E	ΔP
0	0.74	−0.74
1.41	1.14	+0.27
2.82	1.55	1.27
4.22	2.02	2.20
5.63	2.52	3.11
7.04	3.19	3.85
8.45	3.98	4.47
9.86	4.61	5.25
11.26	5.35	5.91
12.67	6.04	6.63
14.08	6.99	7.09

TABLE 15

Fixation of phosphates in very acid solutions in the presence and absence of hydrogen peroxide

Soil no. 7512

	P_I	P_E	ΔP
H_2O_2 not present	239.1	217.4	21.7
H_2O_2 present	242.6	221.3	21.3

titanium solution is added to an acid solution of phosphates containing sufficient hydrogen peroxide. Soil No. 7512 was agitated for 2 hours with two acid phosphate solutions, one of which contained H_2O_2. After filtering, a titanium sulfate solution at pH 0.5 was added to portions of each filtrate. In the one to which no H_2O_2 had been added a precipitate was formed. In the other an intense organge-yellow color, but no precipitate, was formed. The phosphate was then determined in appropriate aliquots. The results appear in table 15. The amount fixed is not so great as in other experiments, since the time of mixing was rather short. It seemed desirable not to allow the H_2O_2 to be too greatly diminished, as might have occurred over a longer period.

It is quite apparent from these facts that the fixation was not due to the

precipitation of titanium compounds. The remaining possibility is that of a sorption.

CONCLUSIONS

Returning to the four hypotheses presented in the introduction, we can eliminate the hypothesis that precipitation by replaced bases plays a dominant rôle in phosphate fixation in these soils because the time for complete equilibria is too great; pronounced fixation takes place in soil freed from replaceable Ca, Mg, etc., and fixation is still very great in very acid solutions in which such phosphates would be soluble. Fixation cannot be largely due to double decompositions because for any given equilibrium phosphate concentration, the amount of phosphate fixed varies very nearly as the ratio of soil to solution; the phosphates are fixed in very acid solutions under such conditions that a double decomposition with calcium, magnesium, manganese, iron, aluminum, or titanium compounds cannot be responsible.

Unless some other possibility remains, we are left with sorption as the only alternative. Between adsorption and absorption, the choice is not so clear. The principal argument against the adsorption hypothesis is the slowness with which equilibrium is attained and reversed. It is possible that a true adsorption may proceed very slowly in some cases, as is true of sorptions by gels, if these are to be considered as adsorptions. In fact, the chief criterion between adsorption and absorption must remain that of the rate of reaction except in two cases: (*a*) A pronounced sorption occurs in a substrate of very low dispersion and (*b*) an examination of the material shows that a new mineral substance has been formed. The latter case has appeared in the results of Ford (6), who was able to show by X-ray analysis that in the fixation of phosphates by Goethite and other minerals a new crystal structure had been achieved. It is not clear that Ford considered his results to be due to absorption. It would seem very probable that they were due to absorption; almost certainly they were not due to adsorption. This method is probably not practicable with complex materials like soils. Nevertheless, the analogy is not at all unreasonable; it would seem very unlikely that if phosphates are absorbed more or less by hydrated minerals of known composition they would not likewise be absorbed by similar hydrated minerals of the soil.

As far as the mechanism of sorption goes, it is possible that there is little or no true distinction between adsorption and absorption of phosphates by minerals. It is very probable that we have to reckon here with attractive forces more akin to those studied in inorganic chemistry than with those present in the case of the adsorption of gases by charcoal (with the exception of the sorption of oxygen). It is believed that this conclusion is in accord with the views of Mattson (12, p. 396, and elsewhere). The author feels that a careful reading of the profound series of papers by Mattson upon the part of those who still ascribe anion fixation almost exclusively to precipitation will cause doubts of that hypothesis to arise. It must, however, be remarked that

very probably in many soils, notably the alkali soils studied by McGeorge and Breazeale (11) and others, precipitation by interaction with alkaline earth carbonates and by replaced bases is of outstanding importance.

The chief distinction between the two types of sorption lies in the deep seated character of absorption. A study of the effect of increased dispersion upon equilibrium with phosphate solutions might enable one to decide whether there is a diffusion into the solid phase. At present, the author feels that all the evidence supports the hypothesis of an absorption, with, of course, some adsorption.

Very tentatively the following picture is suggested to explain phosphate fixation in soils freed from exchangeable Ca, Mg, etc.:

Phosphates penetrate the liquid-solid phase interface and form new compounds with the hydrated minerals, similar to those suggested by Mattson (14, p. 471) or possibly Werner coördination compounds. These compounds have activities which are a function of their mol fractions, and exist in equilibrium with the hydrated minerals and the phosphate compounds. This suggestion seems superior to the idea of a whole series of individual compounds of varying phosphate content. These compounds can be considered as salts and potentially ionized; the anion is of low mobility; the cations, K, NH_4, etc., are interchangeable. Thus we produce an increased base exchange complex. In addition, cations and anions are distributed between the liquid and solid phases in accordance with Donnans' theory. In accordance with this, we should expect the amount of phosphate fixed to be dependent upon the pH of the solution.

Reaction conditions are similar at the interface. Two cases may occur: (*a*) hydroxyl groups oriented outward in a negative surface are replaced by phosphate ions with an increase in negative potential, (*b*) metal ions oriented outward react with phosphate ions so that the latter are oriented outward, thus reversing the potential in the rarer cases when positive colloids are present in the soil (as in acid solutions) or in any event overcoming the mutual flocculation formerly caused by the excess of negative colloids and thus increasing the dispersion.

The exact nature of the compounds formed remains a mystery. Except for illustrative purposes there is little to be gained by the pursuit of the facile art of writing imaginary formulas. The mystery is, however, no greater than that surrounding the specific nature of the interfacial systems studied in colloidal chemistry.

SUMMARY

An intensive study was made of phosphate fixation in two typical upland Hawaiian soils.

Equilibrium between phosphate solutions and soils was attained only after many weeks.

Final equilibrium curves were obtained with one of the materials.

It was shown that the characteristic "adsorption" curves obtained are ambiguous; they might imply any type of reaction.

For any given equilibrium concentration of phosphates, the amounts fixed are proportional to the ratio of soil to solution employed in the experiments. This is held to be a decisive objection to the possibility that the process is due to double decomposition.

Fixation is reversed very slowly. The slow rate of both the direct and indirect processes casts a doubt upon the ascription of the phenomenon to adsorption.

Pronounced fixation occurs in soil from which the replaceable bases have been exchanged for alkali metal ions.

Cations are absorbed along with the phosphate. At various pH values a ratio of 3 equivalents of cations to 1 mol of phosphorus holds approximately.

The degree of fixation is a function of the hydrogen-ion concentration of the solution.

Fixation occurs to a large extent in solutions maintained at a pH of 0.70 to as slow as 0.25.

It is tentatively concluded that phosphate fixation in soils artificially depleted of replaceable bases which can precipitate phosphate is due to absorption of the phosphate by the soil minerals and the formation of equilibrium complexes. In many soils not so depleted this process nevertheless predominates.

A theoretical basis for the fact that the amount of phosphate fixed is dependent upon the pH of the solution is developed in accordance with the Donnan equilibria.

REFERENCES

(1) AYRES, A. 1934 Phosphate fixation in Hawaiian soils: II. *Hawaii. Planters' Rec.* 38: 131–145.

(2) COMBER, N. M. 1925 The rôle of the electronegative ions in the reactions between soils and electrolytes. *Trans. Faraday Soc.* 20: 1–6.

(3) CRAWLEY, J. T. 1902 Fixation of phosphoric acid in soil. *Jour. Amer. Chem. Soc.* 24: 1114–1119.

(4) DEAN, L. A. 1934 Electrodialysis as a means of studying the nature of soil phosphates. *Soil Sci.* 37: 253–266.

(5) FISHER, E. A. 1922 The phenomena of absorption in soils: A critical discussion of the hypotheses put forward. *Trans. Faraday Soc.* 17: 305–316.

(6) FORD, M. C. 1933 The nature of phosphate fixation in soils. *Jour. Amer. Soc. Agron.* 25: 134–144.

(7) HANCE, F. E. 1933 Phosphate fixation in Hawaiian soils. *Hawaii. Planters' Rec.* 37: 182–196.

(8) LANGMUIR, IRVING 1918 The adsorption of gases on plane surfaces of glass, mica, and platinum. *Jour. Amer. Chem. Soc.* 40: 1361–1403.

(9) LOHSE, H. W., AND RUHNKE, G. N. 1933 Studies on readily soluble phosphate in soils: III. The effect of phosphate treatment. *Soil Sci.* 36: 303–316.

(10) MCGEORGE, W. T. 1922 Phosphate in Hawaiian soils. The combinations and their availability. *Hawaii. Planters' Rec.* 26: 11–27.

(11) McGeorge, W. T., and Breazeale, J. F. 1932 Studies on iron, aluminum and organic phosphates and phosphate fixation in calcareous soils. Ariz. Agr. Exp. Sta. Tech. Bul. 40.

(12) Mattson, Sante 1929 The laws of soil colloidal behavior: II. Cataphoresis, flocculation and dispersion. *Soil Sci.* 28: 373–409.

(13) Mattson, Sante 1929 The laws of soil colloidal behavior: I. *Soil Sci.* 28: 179–220.

(14) Mattson, Sante 1930 The laws of soil colloidal behavior: III. Isoelectric precipitates. *Soil Sci.* 30: 459–495.

(15) Mattson, Sante 1931 The laws of soil colloidal behavior: V. Ion adsorption and Exchange. *Soil Sci.* 31: 311–331.

(16) Mattson, Sante 1931 The laws of soil colloidal behavior: VI. Amphoteric behavior. *Soil Sci.* 31: 343–365.

(17) Midgley, R. R. 1931 The movement and fixation of phosphates in relation to permanent pasture fertilization. *Jour. Amer. Soc. Agron.* 23: 788–799.

(18) Russell, E. J., and Prescott, J. A. 1916 The reaction between dilute acids and phosphorus compounds of the soil. *Jour. Agr. Sci.* 8: 65–110.

(19) Teakle, L. J. H. 1928 Phosphate in the soil solution as affected by reaction and cation concentrations. *Soil Sci.* 25: 143–162.

(20) Vanselow, A. P. 1932 Equilibria of the base exchange reactions of bentonites, permutites, soil colloids and zeolites. *Soil Sci.* 33: 95–113.

(21) Weiser, V. L. 1933 Fixation and penetration of phosphates in Vermont soils. Vt. Agr. Exp. Sta. Bul. 356.

(22) Williams, C. O. 1929 The fixation of phosphates in soils. *Union So. Africa Dept. Agr., Div. Chem., Ser.* 100: 426–438.

A NEW METHOD OF ESTIMATING EXCHANGEABLE BASES IN SOILS

AMAR NATH PURI

Irrigation Research Institute, Lahore (India)

Received for publication August 20, 1934

The importance of exchangeable bases in soils needs no emphasis. It is well known that a large amount of food material in soils for the use of plants resides in the exchange complex and some of the most fertile soils are those rich in exchangeable bases. A knowledge of the nature and amount of exchangeable bases is of prime importance in all studies of the relation between soil conditions and plant growth.

Analytical methods for the estimation of exchangeable bases are tedious and time-consuming. Besides, their accuracy is doubtful in the case of saline, alkali, and calcareous soils. The principle of almost all these methods is the same, i.e., the replacement of exchangeable ions in the soil by a single ion through prolonged leaching with its neutral salt. NaCl, KCl, $BaCl_2$, NH_4Cl, and ammonium acetate in water or alcoholic solution have been suggested by different workers for this purpose. Of these, ammonium acetate is perhaps the most favored because of the ease with which it can be removed from the leachate prior to the estimation of the various bases. Some of the errors involved in these estimations in the case of calcareous and alkali soils are avoided by the use of alcoholic solutions, or by estimating Ca in a second liter of the leachate with the neutral salt and allowing for the soluble $CaCO_3$. All these precautions, however, make the estimations more cumbersome and are adopted with reluctance when a large number of estimations have to be completed in a comparatively short time.

The writer has recently advocated the use of $Ba(OH)_2$[1] or ammonium carbonate[2] for the estimation of exchangeable Na and K in soils. Further work in this direction has shown that in ammonium carbonate we have an extremely useful reagent for the estimation of all the exchangeable ions commonly met with in soils. Its use makes these estimations not only simpler but free from objections that can be raised against other methods. It can be used with success for practically all types of soils.

In order to explain the working of the ammonium carbonate method it is nec-

[1] Puri, A. N. 1933 A new method for estimating replaceable Na and K in soils. *Soil Sci.* 26: 355.

[2] Puri, A. N. Estimation of replaceable Na and K, exchange capacity, and degree of alkalization in alkali soils by ammonium carbonate extraction. To be published in *Soil Sci.*

essary to offer some preliminary remarks on its action on a soil containing all the four exchangeable bases, i.e., K, Na, Mg, Ca. Ammonium carbonate solution replaces from the soil all these bases, which appear as carbonates. However, on account of the limited solubility of $CaCO_3$ in ammonium carbonate solution only K, Na, and Mg, carbonates come in solution and appear in the filtrate. If the filtrate is evaporated to dryness all the ammonium carbonate disappears, leaving behind a residue of K, Na and Mg carbonate with a small amount of $CaCO_3$. Sodium and potassium carbonates can be easily separated from magnesium carbonate, because the first two are soluble in 50 per cent alcohol, the last is not. Since the remaining $MgCO_3$ is mixed with some $CaCO_3$, advantage is taken of the limited solubility of the latter in ammonium carbonate solution, in which $MgCO_3$ is fairly soluble, to separate the two by extracting with N $(NH_4)_2CO_3$.

It is to be remembered that ordinary ammonium carbonate contains some ammonium carbamate which can result in the formation of soluble Ca carbamate. All solutions of this reagent, therefore, must be heated to 60°C.

TABLE 1

Amounts of Mg added to, and recovered from, soil by ammonium carbonate

MG ADDED	MG RECOVERED
*m.e.**	*m.e.**
5	7.4
10	11.9
15	15.6
20	18.9

* Per 100 gm. soil.

before use. Once the solution has been heated to that temperature carbonate does not go back to carbamate on cooling.

The correctness of the foregoing statements in the case of Na and K replacement by ammonium carbonate has been established elsewhere.[2] In the case of Mg it was proved by working with soils which were made unsaturated and to which known amounts of Mg were then introduced in the replaceable form and determined by the ammonium carbonate method. The following example will make the point clear. A black cotton soil of high base-exchange capacity and containing 54 per cent clay was rendered unsaturated by exhaustive treatment with 0.05 N HCl followed by leaching with water and drying. To 10-gm. portions of this soil in water suspension increasing amounts of $MgCO_3$ were added, and the suspension was boiled for 2 hours. It was then leached with 500 cc. 0.5 N $(NH_4)_2CO_3$ solution, and Mg was determined as described under "Detailed description of the method."

Table 1 shows the amount of Mg added and recovered by the ammonium carbonate method. Since solid $MgCO_3$ was weighed and added to the soil there is likelihood of some error being introduced on that account; the two

sets of results, therefore, may be taken as fairly close. In another soil to which 10.5 m.e. of Mg per 100 gm. of soil was added, the amount recovered was 10.4 m.e. and 9.6 m.e. in duplicate. This soil contained 7 m.e. of Na and K and 25 m.e. of Ca per 100 gm.

DETAILED DESCRIPTION OF THE AMMONIUM CARBONATE METHOD

The proposed method is slightly varied according as the soil contains or does not contain $CaCO_3$.

For soils free from $CaCO_3$

Portions of soil weighing 10–20 gm. are leached with 500 cc. of 0.5 *N* $(NH_4)_2CO_3$ in 100-cc. lots. The leachate is evaporated to dryness on a sand bath or in an air oven. The residue is taken up with 50 per cent alcohol and filtered. The filtrate with washings is evaporated to dryness, and the residue, after being dissolved in standard acid and brought to the boiling point, is titrated with standard alkali, brom thymol blue being used as indicator. This titration value gives the amount of exchangeable Na and K. If K is required separately, it can be determined in the liquid after titration by any of the standard methods for the estimation of K.

The residue on the filter paper, after the alcoholic extraction, is leached with *N* $(NH_4)_2CO_3$ warmed above 60°C. The filtrate is evaporated to dryness and titrated with standard alkali after the addition of an excess of standard acid and heating to the boiling point. This titration value gives exchangeable Mg. The residue on the filter paper is dissolved in a little semi-normal acetic acid and mixed with the acid leachate for Ca. This acid leachate, which is obtained by leaching the soil after the ammonium carbonate treatment with 500 cc. of semi-normal acetic acid in 100-cc. lots, contains all the exchangeable Ca, which, in turn, is determined by the usual permanganate method. Alternately a separate 10–20 gm. of the soil may be taken and exchangeable Ca determined by leaching with *N* NH_4Cl or semi-normal acetic acid.

It might be pointed out that the problem of estimating exchangeable Ca in soils free from $CaCO_3$ has never presented any serious difficulty, and almost any method could be used with equal success. It is for soils containing $CaCO_3$ that special precautions have to be adopted to allow for the solubility effects.

For soils containing $CaCO_3$

In this method Ca cannot be determined directly in soils containing $CaCO_3$. The indirect determination is not only simpler but more reliable because of its freedom from solubility effects. The soil on the filter paper, after ammonium carbonate treatment for the estimation of exchangeable Na, K, and Mg, is leached with 500 cc. of 0.2 *N* KCl in 100-cc. lots. The filtrate is discarded. The soil is again leached with 500 cc. of semi-normal ammonium carbonate in 100-cc. lots. The filtrate is evaporated to dryness and taken up with freshly boiled hot distilled water and filtered. The residue on the filter paper

is washed with hot water. If on the addition of water to ammonium carbonate residue, the solution is dark colored some $BaSO_4$ pro-Röntgen is added to it before filtering.[3] The filtrate with washings is titrated residually with

TABLE 2

Replaceable bases in calcarious soils as determined by the ammonium carbonate method with a comparison of exchangeable Ca as determined by the KCl method

SOIL NUMBER	LOCALITY	pH VALUE	REPLACEABLE BASES ($(NH_4)_2CO_3$ METHOD)			REPLACEABLE Ca (KCl METHOD)
			Na and K	Mg	Ca	
			*m.e.**	*m.e.**	*m.e.**	*m.e.**
1	Pusa (Bihar)	8.41	0.15	0.15	3.95	5.10
2	Akola (Bombay)	8.21	2.20	3.95	52.35	49.90
4	Punjab	8.55	0.50	0.85	7.05	6.25
5	Punjab	8.77	0.80	0.70	6.10	6.00
7	Punjab	9.58	6.35	0.55	1.40	0
8	Madras	8.41	0.80	0.70	16.90	16.70
10	Madras	8.71	2.35	0.59	19.16	19.25
11	Madras	8.77	0.85	1.20	21.45	22.25
13	Nagpur C.P.	8.53	1.30	0.85	53.80	49.20
16	Lyallpur (Pb.)	8.74	0.50	0.20	4.10	3.50
17	Kalyanpur (U.P.)	8.20	0.20	0.20	7.80	7.65
19	Burma	8.40	1.40	5.25	19.50	16.80
21	Burma	8.25	0.50	0.65	10.45	8.80
24	Meerut (U.P.)	8.59	0.60	0.50	6.35	4.40

* Per 100 gm. soil.

TABLE 3

Exchangeable Mg in $MgSO_4$-treated fields after 3 years compared with control plots

$MgSO_4$-TREATED FIELDS—NUMBER	EXCHANGEABLE MG, M.E. PER 100 GM. SOIL
225	1.00
207	1.00
217	1.30
219	1.30
CONTROL PLOTS—NUMBER	
221	0.65
222	0.65
227	0.75
211	0.80

standard alkali after excess of standard acid has been added. The titration value thus obtained is equivalent to the total exchangeable bases in the soil, and, if we subtract from it the value for exchangeable Na, K, and Mg already

[3] Very dark colored residues should be ignited before being taken up with water.

obtained, we get the equivalent of exchangeable Ca. Alternately for the total exchangeable bases a separate 10–20 gm. of soil may be taken and immediately leached with 500 cc. semi-normal KCl in 100-cc. lots followed by leaching with semi-normal ammonium carbonate.

If a soil contains $CaSO_4$ but no Na_2SO_4, then before ammonium carbonate leaching some $Ba(OH)_2$ should be added; this converts all the $CaSO_4$ into insoluble $BaSO_4$ and $Ca(OH)_2$. When ammonium carbonate is added, the latter, as well as excess of $Ba(OH)_2$ is converted into carbonates and thus rendered harmless. If, however, the soil contains both $CaSO_4$ and Na_2SO_4 then the latter must be removed by leaching with water before ammonium carbonate treatment. Na_2SO_4 alone has no effect and need not be removed from a soil before estimating exchangeable bases by this method.

In order to see how far this indirect method for Ca agrees with any of the other standard methods, exchangeable Ca was determined in a number of soils and compared with the value for Ca obtained by semi-normal KCl leaching. The leachate was collected in two 500-cc. lots, and Ca in the second leachate was subtracted from the first to allow for the solubility effect. The results of this comparison are recorded in table 2. Considering that the KCl method is admittedly subject to errors due to solubility effects, the agreement is fairly close, and as the whole estimation is reduced to simple titrations the method should commend itself to soil workers for routine analyses in connection with survey work.

As an example of the practical application of the method may be mentioned the results of estimations of replaceable Mg from experimental fields to which $MgSO_4$ was applied 3 years ago. Table 3 shows that Mg-treated fields still contain a slightly larger amount of exchangeable Mg than do the control plots.

SUMMARY

Ammonium carbonate is shown to be a very useful reagent for estimating exchangeable bases in soils.

By the method outlined in the paper the determination of exchangeable bases is reduced to simple titrations, thus making possible such estimations with the minimum of equipment and skill.

The method is especially suitable for the study of saline, alkali, and calcareous soils, which have always presented peculiar difficulties in such estimations.

A COMPARISON BETWEEN THE SUCTION METHOD AND THE CENTRIFUGE METHOD FOR DETERMINING THE MOISTURE EQUIVALENT OF SOILS[1]

GEORGE JOHN BOUYOUCOS

Michigan Agricultural Experiment Station

Received for publication September 17, 1934

In a former communication (2) the suction method was suggested as a simple, rapid, and convenient method for determining the comparative moisture holding power, or moisture equivalent, of soils. The principle of the method consisted of using the suction force of water from a faucet to pull the water from the soil instead of the centrifugal force developed in a centrifuge. Because the method is so simple, convenient, easily available, and inexpensive, it has created considerable interest, and the question has been raised: How do the results of this suction method compare with those of the standard moisture equivalent method as developed by Briggs and McLane (3) wherein the saturated soil is centrifuged at a speed to produce a force 1,000 times gravity?

It is the object of this paper to present the suction method as finally developed upon further investigation, and to compare the results it yields with those obtained by the centrifuge method of Briggs and McLane.[2]

DESCRIPTION OF METHOD

The original suction method has undergone considerable improvement in details of technique. The final procedure adopted consists of filling a small Büchner funnel, 5 cm. in diameter and 2½ cm. in depth, with air-dry soil that has been passed through a 2-mm. sieve. Care is taken to compact the soil by tapping gently the lower end of the funnel against the table. The filled funnel is placed in a beaker into which water is poured until it almost reaches the level of the soil. After the soil has soaked for about 24 hours, the funnel is placed on a suction flask (plate 1), which is then connected either to the filter pump or to the vacuum pump, and suctioned for 15 minutes after all the free or excess water at the top of the soil has disappeared. The funnel is then removed from the suction flask, the soil scraped into a weighed receptable, and its moisture content determined in the usual standard way. During suction,

[1] Journal Article 187 N.S., Michigan Agricultural Experiment Station.

[2] In the comparison of the two methods the writer is indebted to Dr. H. E. Middleton of the U. S. Bureau of Chemistry and Soils, and to Dr. Joseph Oskamp of Cornell University, who kindly ran the moisture equivalent of several soils selected for comparison.

the soil is covered with a tumbler containing a moist cloth to prevent evaporation from the soil.

The percolation of the water under suction is very rapid at first in nearly all the soils, but after 5 minutes it becomes very slow, and at the end of 10 minutes only a drop falls about every 2 to 4 minutes.

In the centrifuge method, approximately a 30-gm. sample is used in the case of all mineral soils, regardless of texture. In the suction method, the attempt was made to maintain the same depth of wet soil and not the same weight of dry soil. When the same weight of dry soil is used, the depth of the soil column will vary considerably, as a result of the different degrees of swelling of the various soils upon taking up water. The same depth of soil column was maintained in the suction method by leveling off the soil even with the top of the funnel after the soil was suctioned for about a minute and had become settled and compacted As a result of following this procedure in respect to depth of column, the weight of soil used varied from about 40 to 85 gm., depending upon the class of soil.

The maximum vacuum pressure produced by the water jet pump on the faucet was about 15 mm., and that of the high vacuum pump, about 4 mm. When the water is suctioned from the soil, however, the vacuum pressure produced by both systems is probably the same, because it is limited in both cases by the vapor pressure of the water. Although the maximum vacuum pressure may not be maintained throughout the experiment, nevertheless the pressure is high, as evidenced by the fact that great force is required to detach the Büchner funnel from the suction flask, because of the vacuum pressure in the flask.

The following three factors appear to exert the greatest influence on the results: (*a*) preparation of the soil sample, (*b*) amount of soil sample used, and (*c*) the compactness of the soil, but especially the last two. Whether the soil is used in lumps and allowed to slake in water into its natural ultimate texture (1) or whether it is mechanically ground fine, makes an enormous difference in the results, especially in the finer textured soils. The use of smaller samples of soils, such as 5 or 10 gm., does not yield satisfactory results. The best and most consistent results are obtained by the procedure finally adopted wherein funnels 5 x $2\frac{1}{2}$ cm. are filled with dry soil which is carefully broken up to pass a 2-mm. sieve, and the soil is compacted by gently tapping the lower end of the funnel against the table a few times. As a result of using larger amounts of soil and compacting it, a high suction pressure tends to maintain itself throughout the experiment.

When the procedure outlined is followed closely, the suction method, whether the water jet pump or the high vacuum pump is used, gives consistent results, duplicate tests usually agreeing within 1 per cent and rarely disagreeing more than 2 per cent.

EXPERIMENTAL RESULTS

Comparison between water jet pump and high vacuum pump

In table 1 are shown the moisture equivalent data as obtained on a number of representative soils by the suction method, using for comparison both the water jet pump and the high vacuum pump. The amount of soil used ranged

TABLE 1

Comparison of moisture equivalent determined by use of water jet pump and high vacuum motor pump

SOILS	MOISTURE EQUIVALENT	
	Water jet pump	Vacuum motor pump
	per cent	*per cent*
Michigan sand	5.3	4.9
Fallbrook sandy loam, 14–27½″	12.3	12.5
Sierra Vista sandy loam, 24–43″	12.0	12.3
Clarion loam surface	15.8	16.1
Bladen loam, 8–15″	15.6	15.5
San Joaquin sandy loam, 0–14″	11.8	12.5
Miles fine sandy loam	24.4	23.6
Colby silt loam, surface	28.0	28.1
Cecil clay loam, 1–8″	20.5	20.9
Pierce sandy loam surface	27.9	27.5
Clarion silt loam, surface	27.7	26.9
Colby silt loam, subsoil	23.3	22.6
Bladen loam, 12–18″	31.9	31.6
Decatur clay, 84″	31.8	31.7
Antioch clay loam, 40–60″	30.9	30.4
Kerwin fine sandy loam, 8–12″	37.7	37.8
Lake Charles clay, surface	37.7	32.0
Susquahanna clay, 2–6″	37.0	36.5
Decatur clay, 10–16″	28.0	28.1
Clinton silt loam	25.1	25.5
Marion silt loam, surface	29.3	28.5
Haldemond clay surface	35.4	34.8
Hagerstown clay loam, 20–30″	40.7	40.5
Irredel loam, 12–16″	47.8	47.1
Copay clay adobe	38.6	37.9
Davidson clay loam, 9-30″	38.7	37.8
Parson's silt loam B	44.1	44.4
Clyde clay	48.7	49.0
Webster silty clay loam, surface	45.7	45.1
Stockton clay adobe	49.1	48.5
Yolo silt loam, 1–18″	48.3	47.6
Lufkin clay, 0–3″	52.3	51.8
Lufkin clay, 10–16″	62.8	61.9
Fargo clay B	55.3	55.0
Marengo clay 48″	70.2	69.3
McKenzie clay, B_2	72.2	71.8

anywhere from about 40 to 85 gm., depending on whether it was a clay or a sand soil. All soils were suctioned for about 15 minutes.

The data in table 1 show the expected variation in moisture equivalent according to the textural composition of the soil. Probably the most interesting fact revealed is the very close agreement between data obtained by use of the water jet pump and the high vacuum pump. It will be noted that the

TABLE 2

Comparison between suction method and centrifuge method for determining moisture equivalent

SOILS	MOISTURE EQUIVALENT		
	Suction Method Bouyoucos	Centrifuge Oskamp	Method by Middleton
	per cent	*per cent*	*per cent*
82–7–3:			
A_1	26.2	25.49	
A_2	24.2	22.15	
B_1	28.6	26.35	
C_1	30.5	29.71	
C_2	13.5	14.70	
132–2–23:			
A_1	21.4	21.54	
A_2	16.9	15.73	
B_1	16.2	17.78	
B_2	26.5	25.25	
OOS–1:			
C_1	31.1	27.3	
Marengo clay 48	70.2	65.7	67.0
Fargo clay B	55.3	49.1	47.9
Fargo clay B, ground fine	60.1		53.2
Michigan sand	5.3	2.1	2.7
Haldemond clay, surface	35.4	31.6	32.1
Haldemond clay, surface, ground fine	39.2	32.9	33.8
Sierra vista sandy loam	12.0	10.5	8.5
McKenzie Clay, B_2	72.2	70.1	64.2
Fallbrook sandy loam, 14½–27½″	12.3	12.3	12.7
Colby silt loam, surface	28.0	27.5	27.4
Lake Charles clay, surface	32.2	29.7	28.7
Copay clay adobe	38.6	35.3	34.1
Lufkin clay, 10–16″	62.8	58.3	56.0
Davidson clay loam, 9–30″	38.7	36.5	33.8
Davidson clay loam, 9–30″, ground fine	43.0		41.9

agreement is within 1 per cent. From this, it can be concluded that either vacuum system can be used for determining the moisture equivalent of soil.

Comparison between suction method and centrifuge method

In table 2 is presented a comparison of the moisture equivalents of various soils, as obtained by the suction method and the centrifuge method of Briggs and McLane.

The comparison in table 2 of the moisture equivalent determined by the suction method and by the centrifuge method shows that in some soils the two methods agree very closely, whereas in others the agreement is not so close. On the other hand, the results by the centrifuge method at the two different laboratories do not agree very closely in all the soils. In general, the suction method tends to give somewhat higher values than the centrifuge method. Indeed, it is rather interesting that the two methods agree as closely as they do, since in the centrifuge method the soil is centrifuged for 40 minutes at a force 1,000 times gravity, whereas in the suction method the soil is suctioned for only 15 minutes at a possible suction pressure of only about 15 mm. Since the centrifuge method is an empirical and not an absolute method and it is very sensitive to variations in technique, as shown by Veihmeyer (6), its disagreement with the suction method in some of the soils probably loses considerable of its significance. In fact, it is believed that the suction method gives a truer comparison in the moisture equivalent between heavy clays and the coarse sands than does the centrifuge method. This is because the sands present no obstacle to the free escape of water during centrifuging, whereas the heavy clays, with high colloidal content, tend to become compacted and thereby impede the rate of water escape, with the result that the sands lose proportionally more water than the clays. In the suction method the clays do not become compacted and they are never waterlocked. The idea that the centrifuge may not give a true comparison in the moisture equivalent between the heavy clays and the sands is further supported by the results of Veihmeyer (5), who found that the field capacity of some sandy soils is appreciably higher than their moisture equivalents. Furthermore, there is some evaporation loss from the soils during centrifuging. Lebedeff (4) found that the evaporation loss amounts to 3.5 per cent in a clay when centrifuged for 5 minutes at a speed equal to 70,000 times gravity. When a sand contains only 5 per cent moisture and loses even 1 per cent by evaporation, its comparison with a clay which contains 70 per cent water and loses 3.5 per cent by evaporation becomes distorted. In the suction method, there is very little evaporation, as the soil is covered with a tumbler containing a damp cloth and the suction is only for 15 minutes. Experimental data show that this loss amounts to only about 0.2 to 0.3 per cent.

Since the suction method as finally standardized is accurate, duplicate tests agree very closely, and since it gives results close to those of the centrifuge method, and since it is simple, rapid, convenient, and easily available, it would seem that it is a useful and desirable method for making a comparison of the moisture holding power of soils, especially in laboratories where the centrifuge method is not available. For comparative purposes, the suction method seems to be as reliable as the centrifuge method.

SUMMARY

The suction method for determining the comparative water holding power of soils, or the moisture equivalent, has been further studied and improved.

The principle of the method consists of pulling water out of the soil by suction or vacuum forces and bringing the water holding power of soils to a comparable basis.

Two different systems were used to produce the suction or vacuum forces: (*a*) the water jet or filter pump, and (*b*) the motor vacuum pump.

The method as finally standardized gives very close agreement in replicate tests.

The water jet pump gives almost exactly the same results as the motor high vacuum pump.

The suction method has been compared with the standard centrifuge method for determining moisture equivalent, and the results show that the two methods agree fairly close in the majority of soils investigated. In general, the suction method tends to give somewhat higher values than the centrifuge method.

It is concluded that since both methods are empirical and give only comparative results, and since the suction method is simple, convenient, rapid, and infinitely more available, it should be of value especially to those laboratories that do not have moisture equivalent machines.

REFERENCES

(1) Bouyoucos, G. J. 1927 The ultimate natural structure of soils. *Soil Sci.* 28: 27–37.

(2) Bouyoucos, G. J. 1929 A new, simple, and rapid method for determining the moisture equivalent of soils and the rôle of soil colloids on this moisture equivalent. *Soil Sci.* 27: 233–241.

(3) Briggs, Lyman J., and McLane, J. W. 1907 The moisture equivalent of soils. *U. S. Dept. Agr. Bur. Soils Bul.* 45: 1–23.

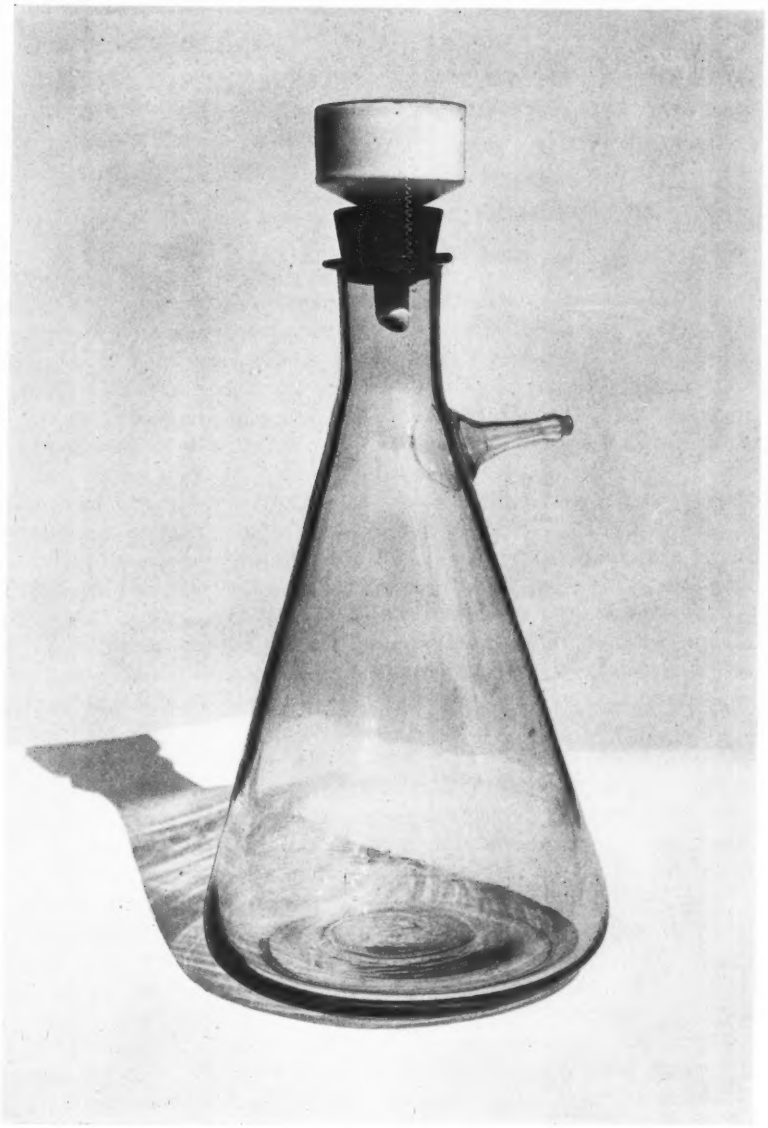
(4) Lebedeff, A. F. 1927 Method of determining the maximum molecular moisture holding capacity of soils. *Proc. and Papers First Internat. Cong. Soil Sci.* 1927: 551–563.

(5) Veihmeyer, F. J. 1931 The moisture equivalent as a measure of the field capacity of soils. *Soil Sci.* 32: 181–193.

(6) Veihmeyer, F. J., Israelsen, O. W., and Conrad, J. P. 1924 The moisture equivalent as influenced by the amount of soil used in its determination. *Univ. Calif. Tech. Bul.* 16: 1–65.

PLATE 1

THE SUCTION METHOD FOR DETERMINING MOISTURE EQUIVALENT IN SOILS



A MACHINE FOR THE SUBSURFACE TREATMENT OF SOILS WITH CHLOROPICRIN AND WITH CARBON BISULFIDE FOR NEMATODE CONTROL UNDER FIELD CONDITIONS

J. R. NELLER AND R. V. ALLISON

Everglades Experiment Station, University of Florida

Received for publication September 17, 1934

Injury to crops by the root-knot nematode (*Heterodera marioni* (Carnu) Goodey is widespread throughout the southeastern United States. Although the problem is receiving considerable attention, the amount of attention is much less than its seriousness should command. At the present time the infestation is becoming increasingly severe in the organic soils of the Everglades where the degree of susceptibility for various crops appears to be somewhat similar to that given by Watson (9) for plants in other regions of Florida. Thus tomatoes, celery, beans, peppers, peas, and other crops of high economic importance are readily attacked.

Among the various lines of approach to this problem undertaken at the Everglades Experiment Station is that of treating the infested fields with chemicals. Even though the cost of chemical treatment is rather high, still it may be feasible for the disinfection of small areas that are to be used for seedbeds. Two of the chemicals that are under trial are chloropicrin and carbon bisulfide. Of these, the latter is the more commonly used in work of this nature.

Recent work with carbon bisulfide in soil treatments has been reported by Lane and Gibson (5) for wireworm control under field conditions, and by Newhall (7) and Guba (3) for the combating of nematodes in greenhouse soils. Chapman (2), Strand (8), and others have used chloropicrin for fumigation of cereal products and household insects. It appears that the earliest use of chloropicrin for soil fumigation was made in England by Mathews (6) who applied the liquid by means of an injector designed for handling carbon bisulfide under similar circumstances. Johnson and Godfrey (4) found chloropicrin to be effective against nematodes in Hawaiian pineapple soil but experienced difficulty[1] with the type of injector employed by Mathews. Similar mechanical difficulties with this type of apparatus were encountered in the present instance. Moreover, the method of application is laborious.

Thus the use of carbon bisulfide and especially of chloropicrin for soil sterilization has been very seriously handicapped by lack of a suitable means of application. Recently a satisfactory method has been developed for the

[1] Private communication.

handling of such chemicals in subsoil treatments, at least under Everglades conditions. Although the experimental work with this machine is only preliminary, it was considered advisable to devote this paper to a discussion of the equipment and procedure in their present stage of development so that their use might be made known to others engaged in root-knot control or allied investigations under various soil conditions. The basic principle of this method suggested itself as a result of the successful use of the mole machine for water table control in the Everglades as discussed in an Annual Report (1) of the Everglades Experiment Station.

DESCRIPTION OF MACHINE

A general view of the experimental machine for the subsoil application of these chemicals is shown in plate 1, figure 1. Its most essential features consist of an iron pipe which is pulled through the soil in a horizontal position at a determined depth by means of a vertical cutter-bar, to which it is attached. The tube which conducts the chemical passes down behind the cutter-bar and into the horizontal pipe. Plate 1, figure 2, gives a more detailed view of the cutter-bar (A), 15 inches long, 2 inches wide, and $\frac{1}{8}$ inch thick; and the attached pipe (B), 8 inches long and 1 inch in diameter. A second pipe of $\frac{1}{4}$ inch diameter is contained inside the 1-inch pipe and extends up the back side of the cutter-bar, to which it is firmly brazed. A flexible hose connects this pipe with the liquid supply tank (C). The outlet for the liquid is through a small hole in a brass spray nozzle cap which is attached to the end of the inner horizontal pipe. This outlet is protected from closure by the surrounding soil by means of a pipe-union (D) which is screwed over the end of the outer 1-inch pipe. The rate of flow is varied by selection of a brass cap perforated by an orifice of the required diameter. The roller (E) compacts the soil into the opening made by the cutter-bar (A).

As shown in plate 1, figure 1, this mole and cutter-bar are pulled through the soil at a determined depth and at a constant speed by means of a tractor, in this case a 3 horse-power Bolens cultivator. Since the machine has a constant rate of movement and a constant rate of liquid ejection, the amount of material desired to be used per acre can be closely controlled. In the experimental machine (pl. 1, fig. 1) the rate of application was still further controlled over rather wide ranges by maintaining a selected pressure in the liquid supply tank, which was equipped with an air pump and a pressure gauge.

For comercial usage it is not necessary to maintain pressure in the supply tank, as the desired variations in rate of application can be obtained with sufficient accuracy by means of adjustment of the size of the orifice outlet; by the rate of movement of the machine; and by the distance between the paralleled lines of application. Furthermore the size of the machine can be varied as desired by attaching a number of units to a draw-bar which also carries the leader-pipe for the liquid conducting system. The energy required for handling the machine in muck soils has been found to be about one horse power

per unit at the draw-bar. Slightly more power was necessary in a sandy soil, however, even though it had been plowed to the desired depth of application. It is important that plowing should precede the applications in order to provide for the rapid and thorough diffusion of the chemicals through the soil.

Another essential feature, shown in plate 1, is a roller to be attached to the dispensing machine. It may also follow as a separate unit to compact the soil into the opening made by the cutter-bar, thereby checking the escape of the vaporized chemical to the air. In some cases it may also be advisable to precede the cutter-bar by a rolling coulter and thus reduce the power requirement. Such a coulter also makes it possible to reduce the width and thickness of the cutter-bar knife, thereby causing less of a soil disturbance above the liquid applications.

TABLE 1

Conditions and results of applications of chloropicrin and of carbon bisulfide by means of the machine described

MATERIAL	TANK PRESSURE PER SQUARE INCH	SIZE OF ORIFICE	DEPTH OF APPLICATION	DISTANCE BETWEEN LINES OF APPLICATION	RATE PER ACRE	INFESTATION ON OKRA PLANTED ONE WEEK LATER
	pounds	*inches*	*inches*	*inches*	*pounds*	
Chloropicrin.....	5	3/64	4, 6 and 9	18	135	Severe
Chloropicrin.....	5	3/64	4, 6 and 9	12	203	Slight
Chloropicrin.....	5	3/64	4, 6 and 9	6	405	None
Carbon bisulfide.....	7	1/16	4, 6 and 9	18	302	Very severe
Carbon bisulfide.....	7	1/16	4, 6 and 9	12	453	Severe
Carbon bisulfide.....	7	1/16	4, 6 and 9	6	906	Moderate

EXPERIMENTAL RESULTS

Table 1 records the factors that were found to be necessary for the application of chloropicrin and of carbon bisulfide at three different rates per acre for each. With chloropicrin an application rate of 135 pounds per acre was obtained with an orifice outlet $\frac{3}{64}$ inch in diameter, a tank pressure of 5 pounds, and the lines of application 18 inches apart. Application rates of 203 and 405 pounds per acre were obtained by reducing the distance between the lines of applications to 12 and to 6 inches, respectively. Carbon bisulfide was applied at the rates of 302, 453, and 906 pounds per acre by limiting the distances between treatments to 18, 12, and 6 inches, respectively, using an orifice of $\frac{1}{16}$ inch and a tank pressure of 7 pounds.

The lateral diffusion of the chemicals in peat was studied by planting an indicator crop of beans in parallel rows 6 inches apart, one directly over the treatment. In general, it appeared that the rows 6 inches to one side of the line of treatment were well protected whereas those 12 inches away were not. This would seem to indicate, therefore, that the lines of application should

be somewhere between 12 and 18 inches apart. Various factors such as type and condition of soil, moisture content, temperature, and severity of infestation would affect the requirements of spacing between the parallel lines of treatment for any given chemical.

The machine has been used successfully to apply chloropicrin and carbon bisulfide at rates varying from 135 to 906 pounds per acre at depths of 4, 6, and 9 inches (table 1). It may be used with any free-flowing liquid or for a combination of liquids prior to, or subsequent to, their arrival under the soil surface. In the latter case two parallel pipes from each of two supply tanks would need to be led down the cutter-bar and into the underground pipe core. Otherwise the ground would have to be gone over twice with a different liquid in the machine each time.

In the case of chloropicrin, the supply tank may be filled and the rate of flow calibrated out of doors with little discomfort if one keeps on the windward side and somewhat above the exposed liquid. The rate of flow is conveniently determined by measuring the amount of liquid that is ejected in a given number of seconds. This factor, together with a knowledge of the speed of the machine, permits a calculation of the amount used per acre for any given spacing between lines of treatment.

When applying chloropicrin it is well to close the outlet valve just before elevating the cutter-bar out of the soil. Preliminary experiments have indicated that the liquid should be liberated at a depth of about 6 inches below the soil surface. In these trials in a peaty soil additional benefits have not been obtained by covering the soil with mulch paper following the applications of the material and the compacting action of the roller.

The experiments were conducted in a field so badly infested with nematodes that susceptible crops such as celery and beans could no longer be grown. No root knot was observed on an indicator crop of okra on the plots treated with chloropicrin at the rate of 405 pounds per acre. There was some infestation where the treatment was at the rate of 203 pounds per acre (table 1), while on the check plots the plants were killed by the root knot. It is believed that the amount of chloropicrin required can be materially reduced by maintaining a thoroughly clean fallow condition in the soil for a longer time before the applications are made. This period of clean fallow should be sufficiently long to insure the complete rotting and disintegration of the root masses, otherwise they will offer sufficient protection to the nematode population harbored in them to defeat the sterilizing effect of the chemical.

Only those chemicals can be used that have a transient existence in the soil, for as long as a chemical is toxic to the nematode it is very likely to be toxic also to plant growth. For this reason the importance of having the root masses well rotted cannot be over emphasized. All weed growth should be avoided also, as some of the common weeds are active hosts for root-knot organisms. It is possible that a crop not susceptible to root knot may be grown during this period of preparation for chemical treatment, but it is not known that this point has been verified experimentally.

Preliminary experiments have indicated (table 1) that over three times as much carbon bisulfide as chloropicrin is necessary for an equall contro of the nematode *H. Marioni.* In addition, because of its fire and explosive hazard by either free flame or by friction, carbon bisulfide is inconvenient to handle. Because of its high vapor pressure, carbon bisulfide in an air-tight container should not be left exposed to the heating effects of the sun's rays. Such an exposure tended to cause the pressure in the supply tank of the dispensing machine (pl. 1, Fig. 1), even though painted white, to be materially increased above that required for the desired rate of flow. The effect was largely prevented by keeping the tank covered with wet burlap bags.

Either chloropicrin or carbon bisulfide is suitable from the standpoint of after effects in the soil, as plants grew normally when seeded within about a week after the treatments. In view of the particularly favorable results with chloropicrin it is to be hoped that a quantity demand for it for soil sterilization purposes will reduce its cost to a point where it may be economically possible to use it on a field scale larger than small seedbed areas.

In the case of the truck crops that are transplanted from seedbeds it is vital that the young plants should be free from root knot, for the reason that a plant already affected by an actively developing disease has less chance for normal growth when placed either in a clean or in an infested field. It is in the sterilization of seedbeds, therefore, that chloropicrin probably will be used first, and the dispensing machine described is well adapted for such usage.

It is obvious, also, that other solutions may be distributed by this type of equipment in the combating of other soil infestations whether of a fungous or an insect character.

SUMMARY

A machine based upon the mole principle has been developed whereby chloropicrin and other disinfecting liquids may be applied in a continuous manner beneath the soil surface. The rate of flow is calibrated from a knowledge of the speed of the equipment and of the amount of liquid ejected per unit of time. Chloropicrin can be applied conveniently by this means and was found more effective than carbon bisulfide in controlling the root knot nematode *Heterodera Marioni* in peat land as measured by the development of crops that are highly susceptible to attacks by the organism.

REFERENCES

(1) ALLISON, R. V. 1928 *Ann. Rpt. Univ. Fla. Agr. Exp. Sta.* 1928: 118.

(2) CHAPMAN, R. N. 1925 Possibilities and limitations of chloropicrin as a fumigant for cereal products. *Jour. Agr. Res.* 31: 745–760.

(3) GUBA, E. F. 1932 Carbon disulfide emulsion for the control of the root-knot nematode. Mass. Agr. Exp. Sta. Bul. 292.

(4) JOHNSON, M. O., AND GODFREY, G. H. 1932 Chloropicrin for nematode control. *Indus. and Engin. Chem.* 24: 311–313.

(5) LANE, M. C., AND GIBSON, K. E. 1932 Carbon disulfide as a control for wireworms. *Jour. Econ. Ent.* 25: 958–967.
(6) MATHEWS, D. J. 1930 Sixth Ann. Rpt. Exp. Res. Sta. Nursery Market Garden Industries, Dev. Soc. Ltd., Turners Hill Chesnut, Herts.
(7) NEWHALL, A. G. 1930 Control of root-knot nematode in greenhouses. Ohio Agr. Exp. Sta. Bul. 451.
(8) STRAND, A. L. 1927 A comparison of the toxicity and the diffusion in a column of grain of chloropicrin, carbon disulfide and carbon tetrachloride. Minn. Agr. Exp. Sta. Tech. Bul. 49.
(9) WATSON, J. R. 1929 The control of root-knot in seedbeds. Fla. Agr. Exp. Sta. Press Bul. 416.

PLATE 1

FIG. 1. General view of the experimental machine showing the liquid supply tank and hose connection with the pipe leading to the subsurface outlet.

FIG. 2. Detail of the dispensing system showing the cutterbar (A), the horizontal subsurface outlet pipe (B), the liquid control valve (C), and the pipe union (D) to protect the orifice outlet from clogging. E is the compacting roller.

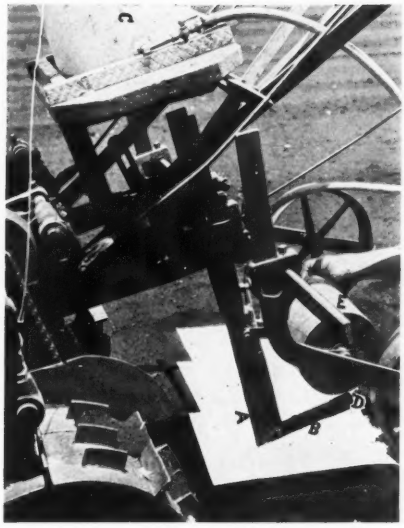


FIG. 1

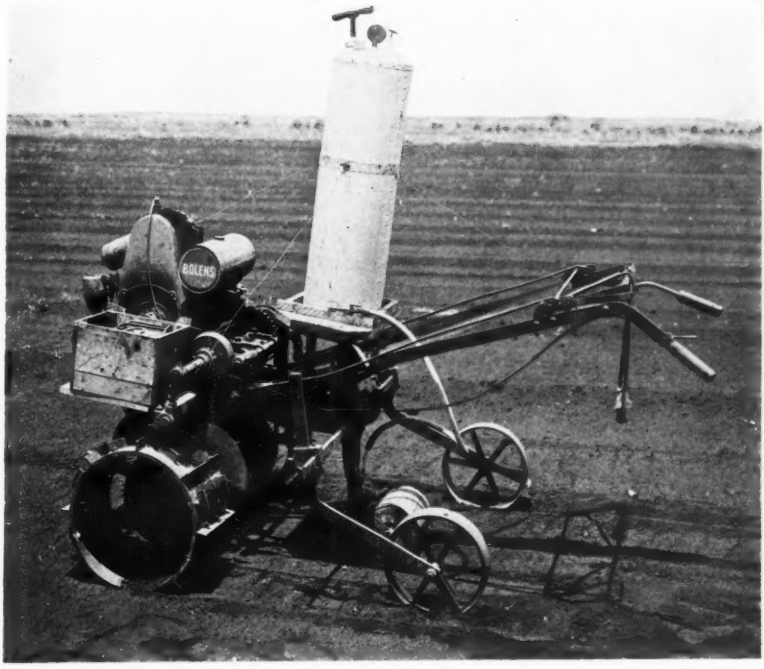


FIG. 2

UNIV. OF MICH.

A COMPARATIVE STUDY OF THE BACTERIAL FLORA OF WIND-BLOWN SOIL: VI. DEATH VALLEY, CALIFORNIA, WITH SUMMARY OF SIX SOIL STUDIES

LAETITIA M. SNOW

Wellesley College

Received for publication August 8, 1934

On February 2, 1933, sand was collected from north and west faces of a bare dune in the northern part of Death Valley.[1] As exceedingly dry sand was anticipated, apparatus for collecting at different depths was not brought, consequently the soil was collected with sterile instruments at approximately 6 inches, the sand scraped away to the 12-inch level, and more sand collected. This was repeated for the 24-inch level, the whole collection being placed in a single container. The 6-inch layer was quite dry, but totally unexpected was the damp condition of the 12-inch and 24-inch layers, due to a storm 10 days previous. The can containing the sand was kept out of doors overnight and carried to Long Beach the next morning by motor and train. It was stored in the vegetable compartment of a Frigidaire overnight and plated the next morning at the University of California at Los Angeles, in Difco nutrient agar, 6 plates each at 1:100, 1:1,000, and 1:10,000 dilutions.

The count was made after incubation at room temperature for 9 days. One hundred colonies were streaked on agar, stored at room temperature for approximately 2 weeks, after which they were carried to the Hopkins Marine Station of Stanford University at Pacific Grove, California, for further study. The methods used in the study of the soil were identical with those of previous studies (18, 19, 20, 21, 22). Nitrate, sucrose, and lactose agar were used instead of broths, and glucose agar was used instead of glucose gelatin, on account of the difficulty in detecting small amounts of acid in glucose gelatin.

CHARACTER OF THE SOILS

Death Valley sand was very fine and uniform in size of grains. All but a few tiny grains passed through the 0.589-mm. sieve of a Tyler Standard Screen

[1] The collection of sand in Death Valley was made possible by the courtesy and assistance of Miss McHendry and Mr. Stacy, Hunter-Clarkson courier and driver, to whom my sincere thanks are presented. I wish also to express my thanks to Prof. T. D. Beckwith of the department of bacteriology of the University of California at Los Angeles, and his assistant, Miss Kosht, who most kindly lent apparatus and furnished media and laboratory facilities, without which the work would not have been possible. As the greater part of the study was carried on at the Hopkins Marine Station of Stanford University at Pacific Grove, California, I wish to present my sincere thanks to Director W. K. Fisher for the courtesy extended to me, and especially to Dr. C. B. van Niel, in whose laboratory the work was done.

Scale, approximately 1 per cent remained on the 0.295-mm. sieve, 92.41 per cent remained on the 0.104-mm. mesh, and the remaining 6.42 per cent passed through the latter.

TABLE 1

Precipitation and temperatures for 5 years previous to study (23, 24, 25, 26, 27)

SECTION	LOCALITY	PRECIPITATION		TEMPERATURES	
		Average annual	Variation	Average mean annual	Variation
		inches	*inches*	*°F.*	*°F.*
Fresh water	Hobart, Ind.	33.10	28.72–38.20	50.06	−20–102
Atlantic coast	Provincetown, Mass.*	37.95	32.88–42.61	47.10	2– 91
	Beaufort, N. C.	54.83	40.70–73.26	63.96	13– 96
Pacific coast	Del Monte, Salinas, Cal.	11.69	7.21–16.06	55.60	24– 95
Inland	Univ. Arizona, Tucson, Ariz.*	12.20	9.12–18.01	66.50	1–111
	Greenland Ranch Death Valley, Cal.	0.39	0.00– 0.57	75.80†	18–126

* In making a comparative study of the climatological data the reports for these stations seemed more nearly complete than those used in previous reports (18, 19).

† Given for 1929 only.

TABLE 2

Physical character of the six soils

LOCALITY	SIZES OF PARTICLES		WATER CONTENT	WATER CAPACITY	OPTIMUM WATER CONTENT*	RELATIVE WATER CONTENT†	COMBUSTIBLE MATERIAL
	>0.5 mm.±	0.1–0.5 mm.±					
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Lake Michigan	0.77	98.86	2.85	25.00	17.50	10.72	0.33
N. Atlantic	73.94	25.80	2.87	23.50	16.45	12.21	0.27
S. Atlantic	13.40	51.10	2.31	23.00	16.10	10.04	0.45
Pacific	0.49	99.31	2.70	23.69	16.58	11.49	0.07
Arizona	4.19	45.00	2.01	27.70	19.37	7.30	1.90
Death Valley	0.00±	93.38	2.14	29.50	20.65	7.21	0.27‡

* 70 per cent of capacity.

† Percentage of optimum water content present.

‡ On account of a misunderstanding, the combustible material was not burned off until February 7, 1934; during the interval the soil had been kept in a sealed box.

In attempting to compare the physical characters of the six soils, there is some difficulty in finding correlations with the climatic conditions. The Atlantic soils are coarser and have a water content nearer the optimum, and the regions have a higher rainfall than the others, which are inconstant in their order. It is evident that the climates of the two arid areas are most nearly alike. The north and south Atlantic areas are also similar, with the Pacific

area coming in between these two groups. The lake station holds an independent position, having rainfall similar to the north Atlantic, an annual mean temperature between the north Atlantic and the Pacific coast, and the greatest temperature range of all the stations.

From table 3 it is evident that the two desert soils agree in pH and high salt content. Death Valley, long noted for the salt accumulation in its soil, heads the list for total salts, which are predominately chlorides, nitrates, etc.

TABLE 3

Chemical character of the six soils

LOCALITY	REACTION	TOTAL SOLUBLE SALTS	CO_3	SO_4	Cl	NO_3 ETC.
	pH	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Lake Michigan	7.5–8.0	0.0120	0.0005	0.0082	0.0005	0.0028
N. Atlantic	6.8–7.2	0.0070	0.0050	Trace	Trace	0.0020
S. Atlantic	9.0–9.2	0.0107	0.0059	0.0016	0.0006	0.0028
Pacific	5.9–6.1	0.0045	0.0014	0.0005	0.0008	0.0018
Arizona	8.6–9.0	0.0540	0.0100	0.0120	0.0010	0.0350
Death Valley*	8.9–9.0	0.4377	0.0132	0.0383	0.1989	0.1872

* The reaction was very kindly determined by Dr. C. B. van Niel, and the chemical analysis was made by Miss Miriam Dice, the analyst for four of the other samples.

TABLE 4

Average total numbers of organisms and percentages of kinds in the six soils
(Per gram of fresh soil)

LOCALITY	DATE OF COLLECTION	TOTAL COUNT	BACTERIA OR YEASTS	ACTINOMYCETES	FUNGI
			per cent	*per cent*	*per cent*
Lake Michigan	June 27, July 4	17,600	82.80	15.19	2.00
N. Atlantic	September 12	93,700	73.53	24.01	2.56
S. Atlantic	March 30	59,666	99.12	0.61	0.27
Pacific*	July 8, October 10	60,346	53.79	44.72	1.47
Arizona	April 18	1,072,000	46.81	52.40	0.77
Death Valley	February 2	17,800	89.32	10.11	0.56

* Averaged for the two collections.

It also has the highest carbonate content of the six soils. Arizona follows, but with noticeably low chlorine content and high percentage of nitrates, etc. The two Atlantic soils are closely alike except for the pH, which is difficult to explain from the figures given. The Pacific sand was the only acid soil studied; it had more CO_3 than the Lake Michigan sand but was noticeably lacking in soluble salts. In appearance it seemed to be almost pure silica sand.

On the assumption that 21°C. and evenness of temperature, moderately fine

soil grains (0.1–0.5 mm.), optimum water content, abundance of rain, pH 7, combustible material, and low soluble salt content are favorable factors, the soils were graded on these characters and the numbers were added; the lowest indicating the most favorable conditions. From these grades the stations arrange themselves in the following order: north Atlantic 22, south Atlantic 23, Pacific 24, Lake Michigan 28, Arizona 30, and Death Valley 36.

PLATE COUNTS

The plates of Death Valley soil were counted first without a lens, bacterial colonies checked with a hand lens, and actinomycetes with a 16-mm. objective. The numbers on the 1:10,000 dilution plates were too few to be accurate and were therefore not included in the results.

From tables 1, 2, 3, and 4 there seems to be no clear correlation between the environmental factors and the total number of organisms nor between the proportions of the various kinds. The two arid regions are nearly at the two ends of the series as to numbers. The region with the highest annual rainfall (S. Atlantic) has a total count very close to a region (Pacific) with only 11.59 inches per annum. How far this lack may be compensated for by the Pacific fogs cannot be stated.

The results of Khalil's work (15) showed that drying reduced numbers but that dried soil moistened had higher numbers than permanently moist soil, due to better availability of organic matter. This suggests a reason for the high count in Arizona, which had also a comparatively high percentage of combustible material. The low number in Death Valley is not entirely an exception to this correlation, since this soil had little organic matter.

The proportion of fungi appears to follow, not climatic factors, but rather roughly the pH. Arizona, Death Valley, and south Atlantic soils all are poor in fungi and have high pH values. The highest count for fungi, however, is not in the most acid soil (Pacific) but in the one most near neutrality (north Atlantic). The high counts for actinomycetes were in the Pacific and Arizona soils, which were dry but not the driest, one acid and one basic. The lowest count for this group was in a basic soil (south Atlantic) which had the highest rainfall of the series. If low rainfall were solely responsible for high numbers, however, north Atlantic soil should not have approximately 9 per cent more actinomycetes than Lake Michigan soil. Jensen (13) is of the opinion that pH, except for highly acid soils, has no effect on numbers of actinomycetes, and gives, in his second paper (14), pH 5–6 as the critical point. This would make the Pacific soil just at the critical point, but not below it. Death Valley and Lake Michigan soils have approximately the same percentage of actinomycetes as was found by Brown and Benton (1) for Iowa (12.45 per cent) although the conditions in the three habitats are quite different. It is not possible to compare Dixon's results (4, 5) as her media were purposely made acid (pH 4.6) to cut down the bacteria on her plates.

SEASONAL VARIATIONS

In discussing numbers of bacteria and climate it must not escape notice that, although an attempt was made in each case to get representative samples of soil, these collections were made usually only once and at different seasons of the year. There seems to be a great difference of opinion regarding the peak, or peaks, in the curve of yearly variation in numbers of soil organisms, due undoubtedly to the fact that many different factors entered into the different experiments.

Waksman (28) found that the peaks varied with the type of soil and the depth, and did not correlate with moisture. Cutler, et al. (3) found a maximum in November, a minimum in February or March, and a secondary peak at the end of June. These did not correlate with seasonal changes in soil moisture, rainfall, or soil temperature. Erdman (7) found that the peaks in two years were not the same; in one year there was a low in February or March, in the other, a second peak in these months. The maximum for both years was in June, and the minimum in August. These did not correlate with water content. Brown and Halversen (2), working with cropped and fallow land, found a great difference in the curves and concluded that factors other than seasonal ones controlled the numbers. Fehér (9, 10, 11) found that in pine woods and underbrush the peak came in July, whereas in Robinia steppe forest it came in September, this habitat being too hot and dry in July for the best development of organisms. The minima were in January or February. He considers (12) rainfall not so important as temperature but speaks of the complicated interaction of factors, which is evident from a study of his curves. The peaks of Rivas' curves (17) were in September or October, with the low point in November in nine cases and in February in one. Secondary peaks came in April or March. On the whole, his curves seem to correlate with those for temperature.

Fabricius and Feilitzen (8) claim that numbers agree with soil temperature, but the figures seem much too irregular for such a correlation. A similar correlation is indicated by Fehér (9) in attributing the maximum to the energy to the sun, as against rainfall or reaction of soil. On the other hand, Dixon (4, 5) considers rainfall before collection of more influence than temperature. Her work, done in Australia, reverses the seasons, and was not for complete years. Contrary to her claim, Newton (16) found three peaks between May and October, two corresponding to low and one to high moisture.

Considering the times of collection of the six soils herein reported, we find that February, which seems to have given more minima than maxima, may be a factor in the low count of Death Valley sand, but seasonal variation could not alone account for the low count in Lake Michigan soil, since no minima, but almost universally maxima, have been reported for June and July. April has been reported for a maximum in one case and this for cropped soil (2), which is difficult to correlate with the high count in Arizona.

COLORED FORMS APPEARING IN THE SIX SOILS

Colors would seem to correlate more closely with chemical than with physical factors but a study of tables 3 and 5 does not reveal any close relation between the various colors and the pH or proportions of the various soluble salts. The only apparent relation seems to be the almost total lack of colored forms in the acid sand from the Pacific coast, which is poor in soluble salts, as contrasted with the results from Death Valley, which has the highest percentage of soluble salts, high pH, and the highest percentage of colored forms. There seems to be no correlation in the intermediate soils between color and total salts nor the proportions of the individual salts tested.

The high percentage of fluorescent forms in Death Valley is very interesting. At one time it was suggested that the high percentages of such forms in Lake Michigan and north Atlantic soils might be due to the proximity of large bodies of water, as contrasted with the low numbers in Arizona (20). But the low figures for south Atlantic, the almost total lack of such forms in Pacific sand

TABLE 5

Percentages of colored colonies on plates of six soils

LOCALITY	TOTAL NUMBER	WHITE	YELLOW	ORANGE	RED	FLUORESCENT	BROWN
Lake Michigan	1,107	83.01	3.07	0.27	0.54	13.09	Few
N. Atlantic	318	75.78	7.23	1.57	0.94	14.46	Few
S. Atlantic	1,210	83.17	8.22	0.49	0.70	7.42	0.00
Pacific	3,850	99.14	0.54	0.10	0.00	0.21	0.00
Arizona	360	88.33	6.39	0.28	1.11	1.39	2.50
Death Valley	1,028	57.10	14.10	1.84	0.39	26.46	0.09

and the very high numbers in Death Valley would be a direct argument against this suggestion.

MORPHOLOGY AND PHYSIOLOGY OF SELECTED CULTURES

The 100 cultures isolated from Death Valley plates were tested for purity by repeated plating. In some cases this proved a difficult process, as two kinds of colonies continued to appear on the plates. After a long series of plates it was decided that the mucoid colonies with the wavy edges and the rough colonies with granular edges were merely two types of the same form. The cultures were not identified, but some of them agreed with the description and photographs of the two types of *B. mycoides* reported by Dooren de Jong (6), who discusses pleomorphism in this form and cites other references on the subject. About 20 other cultures continued to offer difficulties in purification until the end of the work, and as there was a question regarding their condition these forms have been omitted from this report.

In compiling table 6 the slides of the previous work were restudied in the light of subsequent study. In some cases forms previously assigned to yeasts were

thought to be more fittingly placed among pleomorphic bacteria. This rearrangement will alter the percentages slightly but will give a more correct comparison. With the exception of the California soils the percentage of gram-positive forms is fairly uniform. The south Atlantic soil stands out rather conspicuously in morphological peculiarities. The high percentage of coccus,

TABLE 6

Morphology of cultures picked for study in six soils

LOCALITY	TOTAL NUMBER	COCCUS OR COCCOID	PLEOMORPHIC FORMS	NON-PLEO RODS		YEASTS	GRAM'S STAIN			
				Spores	No spores		Total number	+	Variable	−
		per cent	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*	*per cent*
Lake Michigan	102	13.72	10.78	19.60	53.92	1.96	89	31.81	3.40	64.77
N. Atlantic	76	22.36	18.43	15.79	42.10	1.31	61	38.33	1.67	60.00
S. Atlantic	119	31.10	26.90	0.80	41.20	0.00	119	23.60	9.20	67.20
Pacific	92	11.96	6.52	14.12	65.21	2.17	92	56.52	0.00	43.48
Arizona	60	21.67	8.33	38.33	30.00	1.67	54	35.20	0.00	64.80
Death Valley	78	12.82	5.12	33.33	48.72	0.00	78	56.41	14.10	29.49

TABLE 7

Physiological characters of organisms from six soils

LOCALITY	NUMBER	FERMENTERS OF				DIGESTERS OF		REDUCERS OF NITRATES
		Glucose only	Glucose Sucrose	Glucose Lactose	Three sugars	Gelatin	Casein	
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Lake Michigan*	79	7.59	17.72	0.00	3.79	70.83	32.05	18.98
N. Atlantic*	61	6.56	19.67	0.00	1.64	59.61	40.00	23.73
S. Atlantic	119	8.40	16.80	0.84	0.00	52.90	26.50	44.60†
Pacific	92	8.69	18.48	4.34	20.65‡	36.95	33.69	20.65
Arizona*	49	8.17	18.37	0.00	2.04	72.55	56.52	30.43
Death Valley	78	11.54	41.03	7.69	21.79	55.13	.....§	30.77

* These tests were not all made at the same time, hence the number of cultures tested differed. In each case the percentages are made from the number tested.

† 7.5 per cent made no growth.

‡ Of this group one culture formed gas in glucose and sucrose but not in lactose. With the exception of the peculiar form noted in the report on south Atlantic soil (21) this was the only instance of gas formation in the whole series.

§ Not tested.

or coccoid, pleomorphic, and gram-negative forms, the total lack of yeasts, and the almost total absence of spore-formers are noteworthy. As the habitat is one of the most favorable of the series, these peculiarities cannot be due to rigorous conditions. Death Valley, standing at the other end of the habitat series, also lacked yeasts, but showed a very high percentage of spore-formers.

This latter characteristic might be due to the difficult conditions for life and is probably to be expected in arid soil. On the other hand, the lack of spore-formers in the south Atlantic sand cannot be due solely to favorable conditions, since the north Atlantic sand, with similarly favorable conditions for life, contained approximately 15 per cent of spore-formers. The presence of water-insoluble carbonates, which has been commented upon in another place (21), may be an important factor.

Although the high percentage of spore-formers was to be expected in arid soils, the surprising point is the relatively large numbers of non-spore-formers that can endure the conditions, presumably severe for bacteria, which exist in these areas.

The great fermentative activity of the Death Valley forms is to be noted in table 7. This does not appear to be due to habitat conditions, however, since Arizona forms agree, not with those from Death Valley, but with Atlantic and Lake Michigan cultures. Protein digesters are fairly low in Death Valley, but high in Arizona. The rather high percentage of nitrate reducers in arid soils might correlate with the high percentage of these salts were it not for the fact that the highest percentage of these forms appeared in south Atlantic soil, which contained the same percentage of these salts as did Lake Michigan sand which showed the lowest percentage of reducers.

NITROGEN FIXATION

At the beginning of the work an attempt was made to isolate Azotobacter from Death Valley soil. Two sets of flasks containing nitrogen-free media were set up, one with sodium molybdate and the other without. One of each set was placed in the window on a warm plate and one in the dark at 25°C. After 3 to 4 days a film started to form on the bottom of the molybdate flask in the light. At the end of 3 weeks additional soil was added to the flasks to hasten growth, which resulted at the end of 6 weeks in a very heavy bottom film and a thin, paraffin-like film on the surface of the molybdate flask in the light, the liquid becoming cloudy. That in the dark, and those without molybdate had no surface film and the latter group no clearly discernable film of any kind; the liquid remained clear.

Microscopic examination showed no Azotobacter cells, but abundant spore-formers. Cultures were streaked off and brought to Wellesley in order to test their ability to fix nitrogen. These cultures were exceedingly difficult to purify. It was also difficult to find, after several months' culture, a suitable medium on which to obtain sufficient growth for the test. In a few cultures, however, tested by the micro-Kjeldahl method, there seemed to be a very small amount of nitrogen fixed.[2] The writer hopes to be able to continue this work.

[2] This work was done by a senior, Edith Levy Elsas. The nitrogen fixation test was made in the Chemical Laboratory of Wellesley College under the direction of Associate Professor Ruth Johnstin.

SUMMARY

Data from drifting sand collected in Death Valley, California, are compared with similar data from sand collected in the following localities: Arroyo bank, near Tucson, Arizona; dunes at Sandwich, Massachusetts; south shore of Lake Michigan, Indiana; Shackleford Bank, Beaufort, North Carolina; and the Pacific side of the Monterey Peninsula, California. These data have been published, but in some instances have been revised and rearranged for purposes of comparison.

It was not possible to find clear correlation between conditions of habitat and bacterial numbers or activity except possibly in the case of colored forms, which were almost totally lacking in the acid, salts-poor sand of the Monterey Peninsula and exceedingly abundant in the basic, salt-impregnated soil of Death Valley.

Death Valley has the driest, hottest climate of the series and fine-grained, very dry soil with pH 9 and a large amount of soluble salts.

The plate count was low, 10 per cent of which were actinomycetes. A few fungi appeared. A great abundance of colored forms appeared, with fluorescent colonies the most abundant, followed by yellow.

One third of the cultures selected for study were spore-formers and approximately one-half were gram positive. No yeasts, but a small percentage of pleomorphic forms, were found.

Great fermentative activity was evident, with average amount of protein digestion and nitrate reduction. No Azotobacter was found.

REFERENCES

(1) Brown, P. E., and Benton, T. H. 1927 Microörganisms in some soil profiles in Iowa. *Proc. First Internatl. Cong. Soil Sci.* 3: 100–106.

(2) Brown, P. E., and Halversen, W. V. 1919 Effect of seasonal conditions and soil treatment on bacteria and molds in soil. *Iowa Agr. Exp. Sta. Res. Bul.* 56: 251–278.

(3) Cutler, D. Ward, Crump, Lettice M., and Sandon, H. 1922 A quantitative investigation of the bacterial and protozoan population of the soil with an account of the protozoan fauna. *Royal Soc.* [*London*] *Phil. Trans. Ser. B.* 211: 317–350.

(4) Dixon, D. 1928 The microörganisms of cultivated and bush soils of Victoria. *Aust. Jour. Exp. Biol. and Med. Sci.* 5: 223–232.

(5) Dixon, D. 1930 The microörganisms of the tertiary red sands near Melborne, Victoria. *Aust. Jour. Exp. Biol. and Med. Sci.* 7: 161–169.

(6) Dooren de Jong, L. E. den 1933 Ueber Bacillus mycoides und den Pleomorphismus. *Arch. Mikrobiol.* 4 (1): 36–53.

(7) Erdman, L. W. 1928 The numbers of microörganisms in Carrington Loam as influenced by different soil treatments. *Iowa Agr. Exp. Sta. Res. Bul.* 109: 233–258.

(8) Fabricius, Otto, und von Feilitzen, H. 1905 Ueber den Gehalt an Bakterien in jungfraülichem und kultiviertem Hochmoorboden auf dem Versuchsfelde des Schwedischen Moorkulturvereins bei Flahult. *Centbl. Bakt.* (II) 14: 161–168.

(9) Fehér, D. 1929 Untersuchungen über den zeitlichen Verlauf der Bodenatmung und der Mikrobentätigkeit des Waldbodens. *Biochem. Ztschr.* 206: 416–435.

(10) FEHÉR, D. 1929 Untersuchungen über den N-Stoffwechsel des Waldbodens. *Biochem. Ztschr.* 207: 350–360.
(11) FEHÉR, D. 1930 Mikrobiologische Untersuchungen über den Stickstoff-Kreislauf des Waldbodens. *Arch. Mikrobiol.* 1: 381–417.
(12) FEHÉR, D. 1930 Untersuchungen über den zeitlichen Verlauf der Mikrobentätigkeit im Waldboden. *Arch. Mikrobiol.* 1: 464–492.
(13) JENSEN, H. L. 1930 Actinomycetes in Danish soils. *Soil Sci.* 30: 59–77.
(14) JENSEN, H. L. 1931 The fungus flora of the soil. *Soil Sci.* 31: 123–158.
(15) KHALIL, F. 1929 The effect of drying on the microbiological processes in soils. *Centbl. Bakt.* (II) 79: 93–107.
(16) NEWTON, J. D. 1930 Season fluctuations in numbers of microörganisms and nitrate nitrogen in an Alberta soil. *Sci. Agr.* 10: 361–368.
(17) RIVAS, D. 1911 Bacteria and other fungi in relation to the soil. *Contrib. Bot. Lab. Univ. Penn.* 3: 243–274.
(18) SNOW, LAETITIA M. 1926 A comparative study of the bacterial flora of wind-blown soil: I. Arroyo bank soil, Tucson, Arizona. *Soil Sci.* 21: 143–161.
(19) SNOW, LAETITIA M. 1927 A comparative study of the bacterial flora of wind-blown soil: II. Atlantic Coast sand dunes, Sandwich, Massachusetts. *Soil Sci.* 24: 39–48.
(20) SNOW, LAETITIA M. 1927 A comparative study of the bacterial flora of wind-blown soil: III. Lake Michigan sand dunes, Indiana. *Soil Sci.* 24: 335–342.
(21) SNOW, LAETITIA M. 1935 A comparative study of the bacterial flora of wind-blown soil: IV. Shackleford Bank, North Carolina. *Soil Sci.* 39: 227–231.
(22) SNOW, LAETITIA M. 1935 A comparative study of the bacterial flora of wind-blown soil: V. Monterey Peninsula, California. *Soil Sci.* 39: 233–236.
(23) U. S. Dept. Agr., Weather Bureau. Climatological Data, Arizona Section. 1918–1922.
(24) U. S. Dept. Agr., Weather Bureau. Climatological Data, New England Section. 1920–1924.
(25) U. S. Dept. Agr., Weather Bureau. Climatological Data, Indiana Section. 1920–1924.
(26) U. S. Dept. Agr., Weather Bureau. Climatological Data, North Carolina Section. 1926–1930.
(27) U. S. Dept. Agr., Weather Bureau. Climatological Data, California Section. 1928–1932.
(28) WAKSMAN, S. A. 1916 Bacterial numbers in soils at different depths and in different seasons of the year. *Soil Sci.* 1: 363–380.